

Table II shows that, at 5.6% conversion of cyclooctene at 70° and an average of 60 p.s.i.g. of oxygen, 40% of the alkene reacting is converted to epoxide, 18% to cyclic hydroperoxide, alcohol, and ketone, 24% to residue, and 15% to suberic aldehydes and acids. At 21% conversion at 95° and about 1 atm. of oxygen, 65% of the alkene appears as epoxide,¹⁹ 10% as cyclic hydroperoxide, alcohol, and ketone, 24% as high-boiling materials containing acid, alcohol, and ester groups, and about 1% as CO and CO₂. Thus, the higher temperature and conversion together have sharply increased the yield of epoxide at the expense of the suberic derivatives, but the poor definition of the residue at higher temperatures precludes more detailed discussion.

The 60–70% yields of cyclooctene oxide reported by others^{14,19} deserve further discussion. Each molecule of epoxide formed by addition of RO₂· to cyclooctene (reaction 11) produces an RO· radical which must be converted to another RO₂· radical before the chain can produce more epoxide. (Test calculations indicate that no more than 50% of the oxygen consumed can appear in epoxide.) Each molecule of suberaldehyde²⁰

(20) Our data give no support to the suggestion of de Roch and Balaceanu¹⁹ that the open-chain compounds arise by cleavage of cyclooctenyl-3-oxy radicals to give unsaturated aldehydes, but do not exclude his possibility at higher temperatures.

may indeed provide many conversions of RO· to RO₂· as it is oxidized to carbon oxides, but we are left with a serious selectivity problem. Our data indicate that about 70% of the cyclooctene reacting with peroxy radicals reacts by *addition* to give epoxide, the rest by hydrogen abstraction. This restriction alone puts a 70% ceiling on the yield of epoxide at 70°. Further, there is one RO· radical to be disposed of for each RO₂· radical which produces epoxide. The reaction medium is principally cyclooctene, but if many of the RO· react with cyclooctene in any manner, we cannot obtain the stated 65–70% yield of cyclooctene oxide.²¹ Unless much of the epoxide comes from peracids from suberic and lower aldehydes (in which case larger proportions of acids should have been found¹⁹), or unless the effect of temperature is unexpectedly large, or unless there is some other major flaw in our argument above, the data indicate that alkoxy radicals have little tendency to react with cyclooctene at 95° (contrary to our evidence at 70°).

Acknowledgment. Dr. Theodore Mill interpreted the n.m.r. spectrum of the cyclopentene dimer.

(21) From Figure 3 in ref. 19, 78% of the cyclooctene reacting at 106° was converted to epoxide at reaction of 0.067 mole of O₂/mole of initial alkene. Considering the small proportion of by-products available to convert RO· to RO₂·, these results seem unrealistic to us at this time.

The Liquid-Phase Oxidation of Cyclopentene¹

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This work was undertaken to elucidate autocatalysis in the autoxidation of alkenes. Cyclopentene was chosen for study because it gives a high yield of hydroperoxide (75%) at 50°. In benzene solution, the rate of oxidation is first order in cyclopentene. In neat cyclopentene, the rate is half order in azo initiator and first order in added 3-cyclopentenyl hydroperoxide. The rate of initiation by hydroperoxide corresponds closely to its second-order rate of decomposition; it is an efficient initiator of oxidation. The hydroperoxide is more stable in benzene solution and no autocatalysis of the oxidation of cyclopentene is observed in benzene at 50°. Relations between hydroperoxide concentrations and rates of oxidation show that a retarder is formed during the autoxidation of cyclopentene. An intermediate steady rate of oxidation therefore may only represent a transition from initial autocatalysis to later autoretardation.

Introduction

The objective of this work was to obtain some reliable, fundamental information on autocatalysis in

oxidation of alkenes. Our efforts have been directed to cyclopentene at 50° because it oxidizes readily under mild conditions and gives a high yield (75%) of 3-cyclopentenyl hydroperoxide.

In spite of well-recognized autocatalysis in the oxidation of olefins, very little quantitative information is available. Tobolsky, Metz, and Mesrobian² proposed a theory of steady or maximum rates based on equal rates of formation and destruction of initiating hydroperoxide. Although several other workers have cited this paper when they have observed a steady or maximum rate in an autoxidation, this paper is seldom really relevant in regions of kinetic interest. As clearly stated by Tobolsky, *et al.*, their rate becomes steady when the rate of formation of peroxide equals the rate of decomposition of peroxide and the chain length becomes unity; here the conversions may be so high that the assumed constant concentration of hydrocarbon is invalid.

Jackson and Verhoek³ investigated the autoxidation of cyclohexene and concluded that a steady rate of oxidation does not necessarily indicate a steady con-

(1) Support by the Directorate of Chemical Sciences, Air Force Office of Scientific Research, under Contract No. AF 49(638)-1102 is gratefully acknowledged. This work was presented to the Division of Organic Chemistry at the 148th National Meeting of the American Chemical Society, Chicago, Ill., Sept. 4, 1964, Abstracts of Paper, p. 925.

(2) A. V. Tobolsky, D. J. Metz, and R. B. Mesrobian, *J. Am. Chem. Soc.*, **72**, 1942 (1950).

(3) W. E. Jackson and R. H. Verhoek, Report to Air Force Office of Scientific Research by C. E. Boord, TR 58-82, AD 158 384, Armed Services Technical Information Agency, Arlington, Va., p. 1.

centration of hydroperoxide. While neat cyclohexene oxidized at a steady rate of 0.178 mole/l. hr. over 25–95% conversion at 60°, concentrations of hydroperoxide increased from 1.9 up to 4.9 *M* and decreased to 4.0 *M*. More recently, Kamiya, Beaton, Lafortune, and Ingold^{4a} stated that they were able to confirm the Tobolsky scheme in cobalt acetate catalyzed autoxidation of tetralin in glacial acetic acid. However, their work shows considerable variation in peroxide concentration during the long period of steady rate. In neat tetralin or in chlorobenzene solution, the cobalt gradually precipitated and no steady rate was attained.^{4b}

In our related study of the products of oxidation of alkenes,⁵ we found that cyclopentene is among the most reactive hydrocarbons in oxidation at 50°; that it gives a high yield of hydroperoxide (75% of 3-cyclopentenyl hydroperoxide, most of the rest of the product being C₅H₇O₂C₅H₈O₂H); and that the oxidation is strongly autocatalytic. We chose this hydrocarbon to expand our knowledge on rates and autocatalysis in oxidations.

This paper reports the rates of autoxidation of cyclopentene at 50–70°, neat and in benzene solution, initiated by 2,2'-azobis(2-methylpropionitrile) (ABN) and by 3-cyclopentenyl hydroperoxide, and shows that some retarder is formed during the autoxidation. We conclude that the steady rates observed in conventional S-shaped plots of oxygen absorbed against time in many autoxidations do not represent a steady concentration of hydroperoxide but only a transition from initial autocatalysis to later self-retardation and depletion of substrate. These steady rates therefore probably have no special significance and are unsuitable for comparing rates of oxidation.

Experimental Section

Materials. Cyclopentene was obtained from Columbia Chemical Co. and was washed with Fe(NH₄)₂(SO₄)₂ solution, dried, and distilled through a 10-plate modified Podbielniak column; b.p. 43° (760 mm.). Just prior to use, the hydrocarbon was passed over chromatographic grade alumina to remove traces of hydroperoxide. A few experiments were run with cyclopentene donated by the Arapahoe Chemical Co. which, in addition to the above treatment, was refluxed with maleic anhydride. Cyclopentene from both sources appeared homogeneous in gas-liquid partition chromatographic analysis (5-ft. Carbowax column at 25°) except for a small trailing peak of a few tenths of a per cent of the main peak area. The material also appears homogeneous on SF-96 adsorbant. In our hands, both cyclopentadiene and cyclopentane could be detected by the Carbowax column.

Cyclopentenyl hydroperoxide was obtained from ABN-initiated oxidations of the hydrocarbon carried to 5 to 10% conversion, followed by removal of unreacted hydrocarbon at room temperature and 50 mm. The residue was distilled at ~0.1 mm. in a small, one-piece, Claisen-head rig with pot temperatures raised to 50° and the receiver at 0°. A small forerun was dis-

carded and the main body of the distillate, b.p. 30–32°, collected as cyclopentenyl hydroperoxide. Iodometric titrations⁶ typically showed the material to be 93–95% C₅H₇OOH. The remainder of the material is assumed to be the corresponding alcohol, or 3-cyclopentenone, or a mixture of both. No attempts to concentrate the hydroperoxide further were successful. The initiating properties of the hydroperoxide seem to be sensitive to method of preparation and length of time in storage. Highest rates of oxidation were obtained in hydroperoxide-initiated runs in which the hydroperoxide was freshly prepared from moderate (5%) conversion, ABN-initiated oxidations. Distillation through the simple, all-glass Claisen rig apparently gave hydroperoxide of higher titer and initiation rate than material distilled through a spinning-band column.

ABN was Eastman White Label, recrystallized from acetone-methanol. Solvents were reagent grade, distilled and dried before use.

Oxidation Procedure. The solutions to be oxidized were weighed in heavy glass bulbs with inlet stems made of 8 mm. o.d. capillary tubing. The stems were attached to the oxygen tank reservoir through flexible 1/16-in. o.d. stainless steel tubing and either a clamped metal-glass socket joint or (in later experiments) 5/16-in. Swagelok fittings with nylon ferrules. The oxidation bulbs were agitated in a thermostated cell bath (±0.1°) with a wrist-action shaker, and the consumption of oxygen was followed by the pressure drop as read by a gauge attached to the oxygen reservoir. Estimations of pressure drop of 0.1 p.s.i. could be made and, with the volumes of tank and bulb void normally employed, this drop corresponded to ~2 × 10⁻⁵ mole of oxygen.

The solutions were degassed by the usual freeze-thaw procedure before oxygen was admitted to the system. Since the oxygen reservoir was at ambient temperature, the tank temperature (thermometer taped to the side of the tank) was used to correct pressure changes to 27°. At the end of the run the weight gain of the bulb was determined to 0.1 mg. and checked with the O₂ absorbed by pressure change. The two values usually agreed within 3% allowing for the known void space in the apparatus and taking the solubility of oxygen in the liquid phase as 0.014 mole/l. atm. The weight value is assumed to be more reliable but it was available only at the end of a run. Pressures normally varied between 80 and 20 p.s.i.g. in our experiments, but there was no indication that the reaction rate was affected by pressure within this range. Mass spectral analysis of gas sampled from the bulb at the end of a high conversion run showed only small amounts (1–2%) of CO and CO₂.

Rates were calculated by plotting the oxygen uptake against time and taking the slope of the resulting line. In most cases, six to ten points could be taken before the autocatalytic upward curvature of the graph became noticeable. In these cases, the points which appeared to fall on the line (within 0.2 p.s.i.) were treated by least-squares method to obtain the slope and initial rate. For calculations, densities of cyclopentenyl hydroperoxide were assumed to be 0.95 g./ml.

(6) J. P. Wibaut, H. B. van Leeuwen, and B. van der Wal, *Rec. Trav. Chim.*, **23**, 1033 (1954). Where high concentrations (>1 *M*) were being titrated, preliminary dilution of the sample with acetic acid was made. On tetralin and *t*-butyl hydroperoxides the method gives theoretical titers.

(4) (a) Y. Kamiya, S. Beaton, A. Lafortune, and K. U. Ingold, *Can. J. Chem.*, **41**, 2020 (1963); (b) 2034 (1963).

(5) D. E. Van Sickle, F. R. Mayo, and R. M. Arluck, *J. Am. Chem. Soc.*, **87**, 4824 (1965).

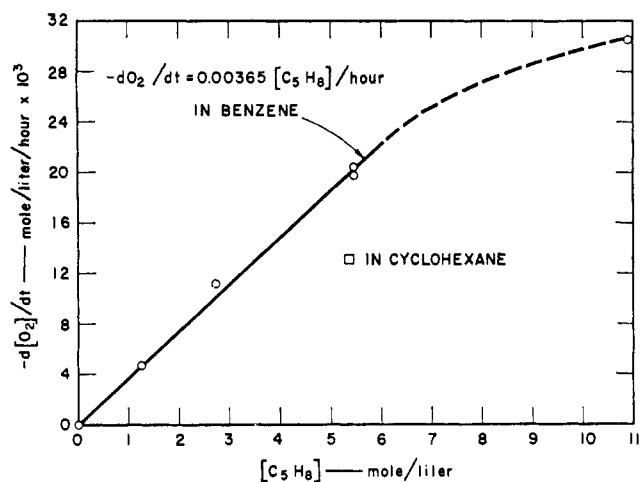


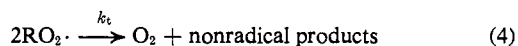
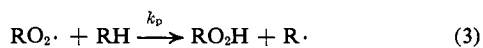
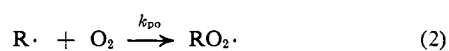
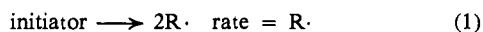
Figure 1. Rate of oxidation of cyclopentene with 0.0096 *M* ABN in benzene (or cyclohexane) solution at 50°.

tene are taken as 0.772 g./ml. at 20° and 0.743 g./ml. at 50°. The latter density corresponds to 10.91 *M* for neat cyclopentene.

Hydroperoxide Decompositions. Solutions of the cyclopentenyl hydroperoxide were made up in the desired solvent, two aliquots were taken to establish the starting titer, and the remainder was pipetted into tubes which were degassed, sealed, and placed in constant temperature baths. The tubes were removed from the bath at appropriate intervals and placed inside heavy-wall flasks which contained the acetic acid, sodium carbonate, potassium iodide, and water of the titration procedure. The tubes were broken with a glass rod and the liberated iodine was titrated.⁶

Postulates and Constants

Conventional mechanisms and expressions and also constants from the literature are collected in this section.



When kinetic chains are long so that oxygen absorbed in chain initiation and evolved in termination may be neglected, and when all alkyl radicals react with oxygen

$$-d[O_2]/dt = -d[RH]/dt = k_p[RO_2\cdot][RH] = (R_i/2k_t)^{1/2}k_p[RH] \quad (5)$$

With initiation by ABN

$$R_i = 2ek_d[ABN] = 2ek_d[ABN]_0 \exp(-k_d t) \quad (6)$$

Here *t* is the elapsed time, and *k_d* for ABN comes from the work of Smith and Carbone.⁷ Their data for 60 and 80° in benzene are summarized by the Arrhenius equation (7) and values of *k_d* which we used at 50–70°

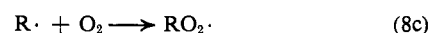
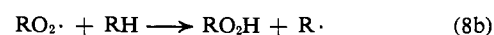
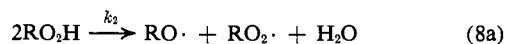
$$k_d = 3.143 \times 10^{15} \exp(-31250/RT) \quad (7)$$

are listed in Table II; *e* is the effective fraction of

(7) P. Smith and S. Carbone, *J. Am. Chem. Soc.*, **81**, 6174 (1959).

radical pairs from ABN which initiates oxidation chains. Our choices of both *k_d* and *e* (0.60) are compromises which are discussed in the Appendix and which may require later revision.

For the decomposition of cyclopentenyl hydroperoxide in cyclopentene, we assume the following reactions, the first being rate determining



In the absence of oxygen and an induced decomposition

$$-d[RO_2H]/dt = [RO_2H]^2 \quad (10)$$

but reaction 8b regenerates hydroperoxide so that a net loss of one molecule produces two radicals (eq. 9). For initiation in the presence of oxygen

$$R_i = 2fk_2[RO_2H]^2 \quad (11)$$

where *f* is the fraction of potential radical pairs which initiates chains.

Rates of Oxidation of Cyclopentene

Many of the experiments in Table I were carried out to establish eq. 5. Over a tenfold change in ABN concentration, oxidation is 0.50 order in ABN. Chain termination is therefore second order in radicals. Experiment 66, where the reaction vessel was packed with glass tubing to increase the surface area, gave the same rate of oxidation as in an unpacked vessel. Thus cyclopentene gives no evidence of a wall effect and first-order termination found with styrene by Howard and Ingold.^{8,9}

Table I and Figure 1 show that the rate of oxidation of cyclopentene in benzene solution is first order in cyclopentene within experimental error. The line in Figure 1 is the least-squares line through the point 0,0 and the four experimental points. This line corresponds (eq. 5) to $(R_i/2k_t)^{1/2}k_p = 0.00365 \text{ hr.}^{-1}$. However, on this basis, the rate of oxidation of neat cyclopentene is only 77% of that expected from the benzene results. One experiment in cyclohexane solution oxidized only two-thirds as fast as a corresponding benzene run and even somewhat slower than expected from the rate in neat cyclohexane. Very similar effects of benzene and cyclohexane have been observed in oxidations of styrene⁹ and cyclohexene.¹⁰

Table II lists values of the composite rate constant, $k_p/k_t^{1/2}$, determined from runs 31 and 3 (50°), 72 (60°), and 74 (70°), and eq. 5 and 6. An Arrhenius plot of these data gives an activation energy, $E_p - E_t/2$, of 6.9 kcal. In a previous investigation, Bolland¹¹ estimated the activation energy for *k_p* as only 9.0 kcal. for an olefin of the degree of substitution of cyclopentene, exclusive of ring strain or other non-bonded interactions.

(8) J. A. Howard and K. U. Ingold, *Can. J. Chem.*, **40**, 1851 (1962).

(9) J. A. Howard and K. U. Ingold, *ibid.*, **42**, 1044 (1964).

(10) D. G. Hendry and G. A. Russell, *J. Am. Chem. Soc.*, **86**, 2368 (1964).

(11) J. L. Bolland, *Trans. Faraday Soc.*, **46**, 358 (1950).

Table I. Oxidation of Cyclopentene^a

Expt. no.	Initial C ₅ H ₈		Volume of soln., ml.	Initial [ABN] (mM), [RO ₂ H], ^b M	O ₂ absorbed, mmoles	RO ₂ H formed, mmoles	Final [RO ₂ H], M	Rate of oxidn., mmole/l. hr.	
	mmoles	M						Initial	Final
No solvent									
78	503	10.91	46.2	0	19.3	16.7	0.36	~2	53
86	548	10.91	50.3	9.62	27.0	23.9	0.48	29.2	79
89	557	10.91	51.2	9.62	53.5	47.5	0.93	30.9	136
57	110.0	10.91	10.12	9.63	9.5	29.4	106
66 ^c	277	10.91	25.5	9.63	18.3	30.4	...
95	489	10.79	45.3	0.10 ^b	23.8	20.9	0.56	21.6	77
129	236	10.72	22.0	0.179 ^b	26.6	22.8	1.22	37.5	164
127	244	10.50	23.3	0.361 ^b	38.4	33.7	1.82	67.8	200
117	224	10.29	21.8	0.588 ^b	24.5	19.8	1.50	97	160
25	90.6	9.83	9.22	0.968 ^b	16.8	176	...
106	84.5	9.76	8.66	1.02 ^b	14.0	10.9	2.29	170	216
113	75.5	8.70	8.68	2.02 ^b	19.5	14.4	3.65	273 ^d	240
157	558	10.91	51.1	0.95	23.8	20.4	0.40	10	60
41	108.2	10.91	10.02	38.5	13.9	56.7	...
46	111.9	10.91	10.37	94.0	19.8	97	...
80	107.3	10.91	9.94	38.5	12.8	~61	...
A86	500	10.69	47.2	0.201 ^b	27.6	24.0	0.72	34.4	93
h	365	10.14	35.8	0.689 ^b	23.1	127	...
Benzene solution									
3	139.0	5.48	25.4	9.63	...	10.0	0.394	20.5	30
31	139.0	5.46	25.4	9.62	16.0	14.8	0.583	19.8	31
5	69.4	2.73	25.4	9.63	...	9.5	0.374	11.2	11.5
43	121.5	1.25	97.1	9.62	26.9	22.7	0.235	4.8	23.2
72 ^e	295	5.43	54.3	9.51	20.9	18.4	0.338	56.9 ^e	74 ^e
99 ^e	57.4	0.63	91.0	9.52	15.3	12.8	0.141	7.3 ^e	1.9 ^e
74 ^f	248	5.36	46.1	9.40	22.1	19.0	0.412	158 ^f	191 ^f
199 ^g	273	5.33	51.1	9.65	10.8	9.6	0.186	13.3	18.1
No solvent, additives as noted ^{h-i}									
11 ⁱ	242	10.8	25.4	9.63	26.5	22.7	0.89	32.6	136
35 ⁱ	92.5	9.23	10.01	0.426 ^b	~17	110	...
70 ^k	247	9.75	25.4	9.62	27.9	11.9	0.47	101	170
57 ^l	100.5	9.95	10.1	9.50	11.8	18.9	1.85	107	154

^a At 50° except as noted. ^b Cyclopentenyl hydroperoxide. ^c Surface area of vessel doubled by packing with capillary tubing. ^d Steady rate observed after 10 min. ^e 60°. For run 99 only, [C₅H₈]/[C₅H₈] was initially 15.95; after 2544 min., 22.23. ^f 70°. ^g Cyclohexane instead of benzene. ^h Continuation after vacuum distillation. ⁱ 0.0549 M cyclopentenone. ^j 0.5663 M cyclopentenol. ^k 1.18 M cyclopentadiene. ^l 0.024 M glutaraldehyde + 0.40 M water added to product of reaction 57 above.

Table II. Effect of Temperature on the Oxidation of Cyclopentene in Benzene

Run	Temp., °C.	[C ₅ H ₈] ₀ , M	k _a , hr. ⁻¹	R _i (eq. 6), mmole/l. hr.	k _p /k _t ^{1/2}
31,3	50	5.47	0.00839	0.0968	0.538
72	60	5.43	0.0358	0.409	0.733
74	70	5.36	0.144	1.62	1.031

Decomposition of 3-Cyclopentenyl Hydroperoxide

Table III summarizes our data on the rate of decomposition of cyclopentenyl hydroperoxide by the procedure of section 2.3. In cyclopentene as solvent at 50°, the decomposition is close to second order (apparently 2.12 up to 0.4 M, then dropping off slightly at higher hydroperoxide concentration) and so eq. 9 is a good approximation. In benzene as solvent, the decomposition is much slower and first order in peroxide; for a 1 M solution, a temperature of about 90° in benzene is required to give the same rate of decomposition observed in cyclopentene at 50°.

Table III. Decomposition of Cyclopentenyl Hydroperoxide

Solvent	Temp., °C.	Initial [RO ₂ H], mole/l.	Initial rate, mole/l. hr. × 10 ³	10 ³ k ₂ , ^a	10 ³ k _{2,12} ^b
				l./mole hr.	or 10 ³ k ₁ ^c
C ₅ H ₈	50	0.0941	0.0418	4.72	3.13 ^b
		0.188	0.180	5.12	3.11 ^b
		0.376	0.789	5.58	3.13 ^b
		0.920	4.38	5.18	2.62 ^b
Benzene	90	0.362	0.941	...	2.60 ^c
Benzene	110	0.352	7.00	...	19.8 ^c

^a Equation 10. ^b $-d[RO_2H]/dt = 2k_{2,12}[RO_2H]^2$. ^c $-d[RO_2H]/dt = k_1[RO_2H]$.

Autocatalysis

We now consider the initiating properties of 3-cyclopentenyl hydroperoxide, first in the initial stage and then at later stages of oxidation of cyclopentene. Figure 2, based on Table I, shows that the initial rate of oxidation of cyclopentene-cyclopentenyl hydroperoxide mixtures is a linear function of the peroxide concentrations up to 1 M peroxide, where about 10% of the cyclopentene has been displaced. When we correct

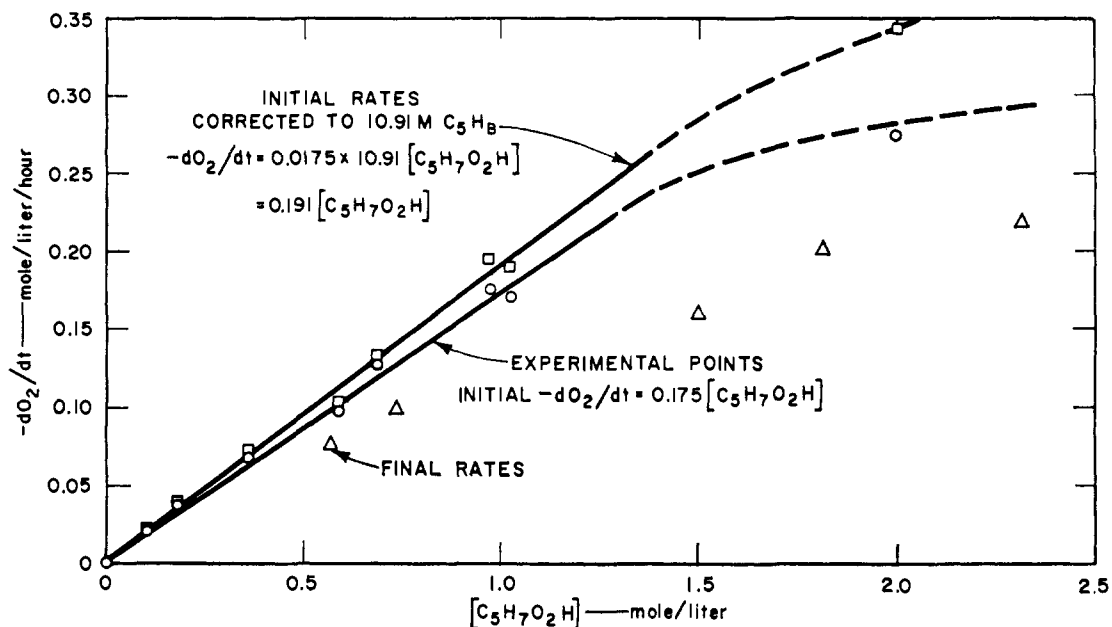


Figure 2. Initial rate of the cyclopentenyl hydroperoxide-initiated oxidation of cyclopentene at 50°

these observed rates to 10.91 *M* cyclopentene, the rate of oxidation is still a linear function of peroxide concentration up to 1 *M* peroxide, but at 2.0 *M* hydroperoxide the rate is 12% less than expected from experiments at lower concentrations. We do not know how much of this lesser rate is due to change in the reaction medium and how much to co-oxidation of hydroperoxide with the olefin. In either case, the rate of initiation (eq. 8a) is strictly second order in hydroperoxide up to at least 1 *M* and eq. 11 is established. Since the decomposition of the peroxide in cyclopentene is also very nearly second order (previous section), the cyclopentene-cyclopentenyl hydroperoxide system is nearly ideal for studying autocatalysis.

Our own experience with cyclohexene is that such integral orders are the exception rather than the rule. Others have reported similar experiences. Jackson and Verhoek³ found that dependence of rate of oxidation of cyclohexene on concentration of cyclohexenyl hydroperoxide varied from 0.75 to 0.85 and that only with neat olefin at 60° was the order near one (0.96). For several systems¹² the rate of oxidation is one-half order in hydroperoxide at very low concentrations but changes to first order at higher concentrations. Decomposition of cyclohexenyl hydroperoxide in cyclohexene is 1.7 order in hydroperoxide.¹³ Hence decomposition is not always a measure of chain initiation, and *vice versa*.

Combining the results in Figure 2 with eq. 5 and 11 gives

$$-d[\text{O}_2]/dt = (fk_2/k_t)^{1/2}k_p[\text{C}_5\text{H}_7\text{O}_2\text{H}][\text{C}_5\text{H}_8] = 0.0175[\text{C}_5\text{H}_7\text{O}_2\text{H}][\text{C}_5\text{H}_8]$$

Similarly, eq. 5 and 6 and the average initial rates of oxidation of neat cyclopentene with 9.62 mM ABN at 50°, 0.0297 mole/l. hr. from Table I, give

$$-d[\text{O}_2]/dt = (0.00962ek_d/k_t)^{1/2}10.91k_p = 0.0297$$

(12) L. Bateman, *Quart. Rev.* (London), 8, 158 (1954).

(13) L. Bateman and H. Hughes, *J. Chem. Soc.*, 4594 (1952).

Dividing the first of these equations by the second, inserting values of k_d from Table II and k_2 from Table III, and solving for f gives for 0.1 *M* peroxide, $f = 0.71e = 0.42$ and for 0.4 *M* peroxide, $f = 0.60e = 0.36$. Thus initiation by cyclopentenyl hydroperoxide seems to be nearly as efficient as by ABN, and high enough to exclude significant chain decomposition.

For oxidations carried to low conversions, this conclusion can be checked from autocatalysis in ABN-initiated runs. If a fixed fraction (x) of oxygen absorbed is converted to hydroperoxide and if the concentrations of hydrocarbon and ABN remain essentially constant, then an equation of the form

$$-d\text{O}_2/dt = a\sqrt{1 + b[\text{O}_2 \text{ absorbed}]^2} \quad (12)$$

should apply, where

$$a = (ek_d[\text{ABN}]/k_t)^{1/2}k_p[\text{RH}] \quad (13)$$

and

$$b = fk_2x^2/ek_d[\text{ABN}] \quad (14)$$

From Table I, $a = \text{initial } R_{\text{O}_2} = 0.0297$ mole/l. hr. for 10.91 *M* C_5H_8 and 0.00962 *M* ABN; b is evaluated from the final oxygen uptake and the integrated form of eq. 12.

$$\text{O}_2 \text{ absorbed} = b^{-1/2} \sinh ab^{1/2}t \quad (15)$$

From experiments 57 and 86, $b^{1/2}$ was evaluated as 4.53 and 4.45, respectively. The average value of b is thus 20.2.

If the fraction of oxygen absorbed which is converted to hydroperoxide, x , is taken as 0.86 in hydroperoxide + dimer, then the value of fk_2 from these experiments is 0.00132/hr., and, for $k_2 = 0.00558$, $f = 0.24$. It is assumed that the rate constant for decomposition of the hydroxide group on the dimer approximates that of the simple hydroperoxide. Since the molar ratio of hydroperoxide to dimer is 8:1, little error in the calculation should be incurred by this approximation. The discrepancy between this and the previous values (0.42–0.36) may be partly due to our difficulties in

establishing precise values for b and x , but it is partly (probably mostly) due to formation of a retarder, to be considered next.

Figure 2 shows initial rates of oxidation as a function of hydroperoxide concentration. The final rates for experiments 95, 86, 117, 127, and 106 (Table I) where the final hydroperoxide titers were determined are also plotted in the figure. These final rates are 80, 78, 63, 73, and 73%, respectively, of those expected from initial rates of oxidation. We have been unable to escape the conclusion that a retarder³ as well as an initiator (hydroperoxide) is formed in the oxidation of cyclopentene. Robertson and Waters¹⁴ have suggested the accumulation of a retarder to explain the near cessation of oxidation of tetralin at high conversions.

In a search for a retarder or its precursors, 3-cyclopentenol, 3-cyclopentenone, water, glutaric dialdehyde, and cyclopentadiene were tested and found to be ineffective (last four experiments in Table I). However, experiment A86 in Table I shows that the retarder is in the nonvolatile products. Distillation of the first oxidation mixture (carried to 5.5% conversion) at 0.1 mm. increased the rate of oxidation from 93 to 127 mmoles/l. hr. even though the peroxide titer of the solution was reduced by distillation from 0.721 to 0.689 mole/l.

The markedly increased stability of cyclopentenyl hydroperoxide in benzene (Table III) offers an opportunity to study autoxidation without the usual autocatalysis. In experiment 5, with 2.73 M cyclopentene, the rate of oxidation was essentially the same after 32.5 hr. as at the start. In experiment 99, with 0.630 M cyclopentene in benzene, retardation outweighed any remaining autocatalysis; after 43.1 hr., when the 28.3% of the cyclopentene and 78.6% of the ABN had reacted, the final rate of oxidation was only 26% of the initial rate instead of 34% expected from eq. 5.

Appendix

Choice of k_d and e . The value of k_d calculated from eq. 7 for 50°, $2.33 \times 10^{-6}/\text{sec.}^{-1}$, agrees well with 2.16×10^{-6} reported by Van Hook and Tobolsky¹⁵ in benzene and toluene and with 2.33×10^{-6} reported

(14) A. Robertson and W. A. Waters, *J. Chem. Soc.*, 1575 (1948).

(15) J. P. Van Hook and A. V. Tobolsky, *J. Am. Chem. Soc.*, **80**, 779 (1958).

for tetralin solution by Kamiya, Beaton, Lafortune, and Ingold.^{4a} The Smith and Carbone⁷ k_d values at 60 and 70°, 9.94 and $39.9 \times 10^{-6} \text{ sec.}^{-1}$, respectively, are a reasonable compromise between the Van Hook and Tobolsky value of $9.6 \times 10^{-6} \text{ sec.}^{-1}$ at 60° value and Russell's¹⁶ value of $11.5 \times 10^{-6} \text{ sec.}^{-1}$, selected from older work on decompositions in various aromatic solvents. The expression of Howard and Ingold⁸ for the decomposition of ABN in styrene, $k_d = 1.99 \times 10^{15} \exp(-30,900/RT)$, predicts $42 \times 10^{-6} \text{ sec.}^{-1}$ for 70°.

Choice of a value for e is less certain since its value apparently depends on solvent, atmosphere, temperature, and method of determination. A possible additional complication is that e will be conversion dependent if the intermediate cyanoisopropylimine of dimethylketene¹⁷ ultimately produces radicals.

The initial investigation of radical production by Hammond, Sen, and Boozer¹⁸ indicated that ~60% of the potential radicals could be trapped in benzene or chlorobenzene with iodine as scavenger. In two later papers,¹⁹ they considered ketenimine formation with both ABN and 1,1'-azobis(1-cyanocyclohexane) (ABC). In degassed solutions, as much as 60% of the ABN decomposed may give ketenimine. In the presence of oxygen, however, the amount of ketenimine is greatly reduced, to zero with ABN and to a maximum of 7% with ABC. Hammond and co-workers state the initial efficiency of radical production at 80°, as measured by oxidation inhibition in chlorobenzene, to be 60% for ABC, 42% for the ketenimine derived from ABC. Since build-up of ketenimine is small under oxygen, the average efficiency of azo compounds should not vary much with conversion in inhibited oxidation of cumene at 60° in various solvents. For chlorobenzene they report $e = 0.68$ and for benzene $e = 0.80$. Finally, Kamiya,^{4a} *et al.*, conclude that the efficiency of radical production by ABN in tetralin oxidation at 50° is 0.65. These considerations suggest that $e = 0.60$ represents a reasonable compromise of present literature values.

(16) G. A. Russell, *ibid.*, **79**, 3871 (1957). The Arrhenius expression in this paper does not give his value of k_d at 60°.

(17) M. Talat-Erben and S. Bywater, *ibid.*, **77**, 3710 (1955).

(18) G. S. Hammond, J. N. Sen, and C. E. Boozer, *ibid.*, **77**, 3244 (1955).

(19) C-H. S. Wu, G. S. Hammond, and J. M. Wright, *ibid.*, **82**, 5386 (1960); G. S. Hammond, C-H. S. Wu, O. B. Trapp, J. Warkentin, and R. T. Keys, *ibid.*, **82**, 5394 (1960).