Addition–Abstraction Competition of Acylperoxy Radicals Reacting with Alkenes. Cooxidation of Cyclohexene and Valeraldehyde[1,2]

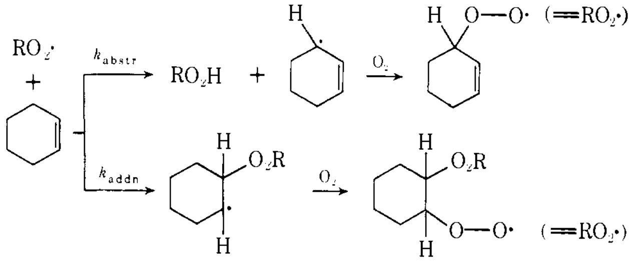
Kenneth E. Simmons and Dale E. Van Sickle*

Contribution from the Research Laboratories, Tennessee Eastman Company, Division of Eastman Kodak Company, Kingsport, Tennessee 37662.

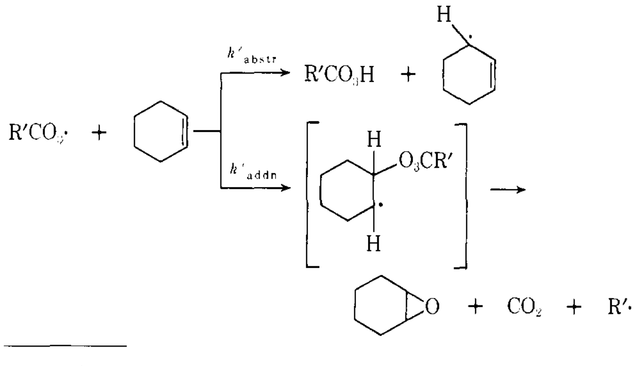
Received January 4, 1973

Abstract: Cyclohexene and valeraldehyde were cooxidized at various feed ratios and, from the product analysis, rate constant ratios were calculated for (1) the relative reactivities of cyclohexene and valeraldehyde toward valerylperoxy and cyclohexenylperoxy radicals and (2) the addition–abstraction reactions of valerylperoxy radicals with cyclohexene. The rate constant ratios (1) indicate that valeraldehyde is more reactive than cyclohexene toward both valerylperoxy radical (by a factor of 1.2) and cyclohexenylperoxy radical (by a factor of 7). The rate constant ratio (2) indicates that addition is 1.5 times faster than abstraction. Since the abstraction–addition rate constant ratio for the attack of cyclohexenylperoxy radical on cyclohexene is 22:1, this work shows quantitatively the greatly altered selectivity of the acylperoxy radical compared to the selectivity of the alkylperoxy radical.

It has been shown that a key step in the mechanism of alkene autoxidation is the addition–abstraction competition of substrates toward the propagating alkylperoxy radical.[3]



Cyclohexene was found to autoxidize almost entirely by the allylic hydrogen abstraction mechanism and 2-cyclohexen-1-yl hydroperoxide was the principal product.[4] In the cooxidation of an alkene and an aldehyde, acylperoxy radicals become significant chain carriers along with the alkylperoxy radicals, and a new addition–abstraction competition enters the oxidation mechanism.[5] The addition of acylperoxy radicals to the double bond apparently yields epoxide directly (along with carbon dioxide and the alkyl radical R′· as coproducts; see the Discussion), and abstraction leads to a peroxy acid and the allylic radical of the alkene substrate.



Due to subsequent nonradical reaction of the peroxy acid with more alkene, epoxide is also a product of the abstraction mechanism; this reaction is well known[6] and has been recently studied by Kwart and Hoffman.[7]

The objective of this work was to measure, from a product study of the cooxidation of cyclohexene and valeraldehyde, the ratio of rate constants for the addition and abstraction reactions, k'_{addn}/k'_{abstr}, of valerylperoxy radicals (R′– = –Bu) reacting with cyclohexene. While previous work suggests that alkylperoxy radicals react preferentially with alkenes by hydrogen abstraction for most substrates, there is evidence from patent literature[8–13] that acylperoxy radicals have a greater tendency to react with alkenes by addition to give epoxides. Some recent publications[14,15] have addressed themselves to the mechanism of the aldehyde–alkene cooxidation reaction. We report here the measurement of some of the ratios of rate constants involved and show in detail how the several possible reactions contribute to the formation of epoxide and other products in the cooxidation of cyclohexene and valeraldehyde at various feeds.

Experimental Section

Materials. Cyclohexene and valeraldehyde (Eastman) were distilled in a nitrogen atmosphere through a 4-ft glass-packed column. The freshly distilled aldehyde was stored in 50-ml screw-cap bottles which were sealed under nitrogen. Valeraldehyde for each experiment was taken from a previously unopened bottle. Just

---

(1) This publication contains information which appears in a portion of the thesis submitted to the School of Graduate Studies, East Tennessee State University, by K. E. S. in partial fulfillment of the requirements for the degree of Master of Science.

(2) Presented to the Division of Organic Chemistry at the 164th National Meeting of the American Chemical Society, New York, N. Y., August 27–September 1, 1972.

(3) F. R. Mayo, *J. Amer. Chem. Soc.*, **80**, 2497 (1958).

(4) D. E. Van Sickle, F. R. Mayo, and R. M. Arluck, *J. Amer. Chem. Soc.*, **87**, 4824 (1965); if epoxide plus 1/2 "dimer" is counted as addition product and all else abstraction, k_{abstr}/k_{addn} is recalculated as 22:1.

(5) T. Ikawa, T. Fukushima, M. Muto, and T. Yangihara, *Can. J. Chem.*, **44**, 1817 (1966).

(6) D. Swern, *Chem Rev.*, **45**, 16 (1949).

(7) H. Kwart and D. M. Hoffman, *J. Org. Chem.*, **31**, 419 (1966).

(8) R. S. Coffey and H. G. Lawley, British Patent 963,430 (1964).

(9) F. Lanos and J. Alagy, French Patent 1,376,471 (1964).

(10) F. Lanos and G. Clement, French Patent 1,401,176 (1965).

(11) J. B. Dickey, *et al.*, French Patent 1,400,305 (1965).

(12) J. Alagy and F. Defoor, French Patent 1,410,985 (1965).

(13) E. A. Blumberg, *et al.*, British Patent 1,080,462 (1967).

(14) A. D. Vreugdenhil and H. Reit, *Recl. Trav. Chim. Pays-Bas*, **91**, 237 (1972).

(15) F. Tsuchiya and T. Ikawa, *Can. J. Chem.*, **47**, 3191 (1969).

Table I. Products from the Cooxidation of Cyclohexene (**2**) and Valeraldehyde (**3**)[a]

Charge data						Oxygen absorption				Products, mmol							
		[3]		[2]		Oxygen consumed, mmol											
Run	Time, min	mmol	M	mmol	M	Wt gain	Calcd	$R_O \times 10^5$, M min^{-1}	$\bar{P}_{O_2}$, psig	Total peroxide	Total acid	Carbon dioxide	Butyl alcohol	Butyraldehyde	Total epoxide	2-Cyclohexen-1-ol	2-Cyclohexen-1-one
31	200	18	0.38	450	9.4	14.6	14.4	1.7	13.0	9.55	1.33	1.88	1.41	0.56	3.04	7.76	1.65
43	167	18	0.38	454	9.4	15.2	15.1	2.1	13.1	9.90	1.47	1.89	1.40	0.35	2.95	8.99	0.82
39	119	35	0.72	438	9.0	16.4	16.2	3.5	12.2	8.96	2.36	2.82	2.58	0.33	5.20	7.48	0.55
26	111	52	1.09	415	8.7	16.4	15.9	3.7	10.5	7.88	3.31	3.47	3.14	0.70	6.63	5.59	0.48
41	105	52	1.09	420	8.7	16.4	16.2	3.9	10.6	8.13	3.42	3.47	3.14	0.51	6.38	5.80	0.40
37	83	75	1.50	397	8.2	19.8	19.2	5.9	12.6	8.59	5.30	4.43	3.91	0.63	8.90	5.65	0.37
33	77	103	2.10	370	7.6	18.3	18.2	6.4	11.1	7.11	6.80	4.04	3.89	0.57	9.04	4.13	0.29
51	50	140	2.86	333	6.8	20.5	18.9	10.9	11.8	6.64	9.54	3.66	4.25	1.02	10.56	3.78	0.26
53	73.5	75	1.50	402	8.2	18.4	16.9	5.6	75.0	8.98	5.78	2.59	3.73	0.27	7.38	5.63	0.18
56[b]	36	75	1.50	402	8.2	20.7	19.9	17.0	11.0	10.45	5.20	3.84	4.75	0.22	9.06	6.90	0.22
57[c]	220	75	1.50	401	8.2	20.1	19.2	2.1	11.9	8.62	5.54	4.45	4.40	0.55	8.39	5.55	0.27

[a] [Initiator] = 0.01 M and temperature = 60°, unless otherwise indicated. [b] Temperature = 70°. [c] Temperature = 50°.

before each experiment, the distilled cyclohexene was passed over alumina to remove traces of any hydroperoxide present.

The initiator 2,2′-azobis(2-methylpropionitrile) (Eastman) was recrystallized from an acetone–methanol solution. Triphenylphosphine (Matheson Coleman and Bell) was recrystallized from 95% ethanol and then sublimed. Pentamethylbenzene (Eastman reagent grade) was used as obtained.

Apparatus. An apparatus for pressuring solutions with oxygen in glass bulbs has been described.[16] Modifications were made to connect the bulbs to the oxygen tank reservoir through 1/8-in. o.d. tubing and to connect a small vacuum manifold to the apparatus. These modifications allowed the bulbs to be degassed before the reaction and aided in removal and collection of product gases in the void space above the liquid.

Cooxidation of Cyclohexene and Valeraldehyde. The solutions of cyclohexene, valeraldehyde, and initiator were weighed into the reaction bulbs; the bulbs were cooled to −80° and degassed, and oxygen at ~10 psig was admitted into the bulbs. The bulb temperature was maintained at −80° overnight, after which the bulbs were warmed to room temperature and then brought to reaction temperature by shaking them in the thermostated oil bath. Additional oxygen pressure was added to give a total of 25 to 30 psig in most experiments. Consumption of oxygen was followed by the pressure drop measured by a gauge attached to the oxygen reservoir. The oxidations were carried out in cycles, so that the solutions were not repressured until all oxygen above the liquid had been consumed.

Oxygen Absorption Calculations. The pressure gauge readings, taken at the ambient temperatures of the reservoir tank, were converted to absolute pressure and corrected to a uniform temperature of 27° for the reservoir by use of an equation which has been described in detail.[17] A plot of the corrected pressures from the end of each cycle *vs.* time gave a measured sum of hydrocarbon and inert gas pressures at any point during oxidation and thus permitted determination of oxygen pressures. It was possible to calculate the quantity of oxygen consumed from these data. (In calculating the oxygen consumption we allowed for the known void space in the apparatus and used for the solubility of oygen in the liquid 0.010 mol/l. atm.) The values obtained from this calculation were checked with those obtained by the determination of oxygen consumption by bulb weight gain (weights of CO_2 degassed were added back for total gain). We calculated the rates of oxygen absorption by plotting the oxygen uptake *vs.* time and taking the slope of the resulting line. The average oxygen pressure for oxidations over several pressure cycles was calculated from $\bar{P}_{O_2} = \Sigma P\Delta t/\Sigma\Delta t$, where P is the average pressure in each cycle and Δt is the time length of the cycle.

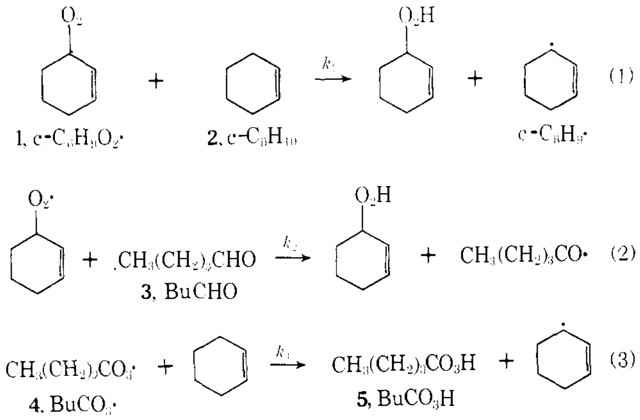
Determination of CO_2. At the end of each run, the reaction was stopped by cooling the bulb contents (−80°). The bulb was degassed at −80°, with the contents being stirred magnetically, through a U-tube trap constructed of 16-mm o.d. glass tubing with pressure stopcocks on both ends. The trap was filled with glass wool and was maintained at −200°. The CO_2 formed in the reaction was collected in this trap and was determined gravimetrically. Small amounts of cyclohexene were also carried over into the trap; correction of the CO_2 weight was made by degassing the trap at −80° with subsequent determination of the weight of cyclohexene.

Product Analysis. The oxidation mixture was analyzed immediately for peroxides by using a common iodometric method.[18] An aliquot of the oxidation mixture was then reacted with excess triphenylphosphine (amount determined from peroxide analysis) to reduce cyclohexenyl and butyl hydroperoxides to the respective alcohols and to reduce any peroxyvaleric acid present to valeric acid. A sample of the reduced solution was analyzed for valeric acid by titration with alcoholic potassium hydroxide. Another sample of the reduced solution was analyzed by gas chromatography after addition of a weighed amount of pentamethylbenzene (internal standard). A 0.25-in. by 16-ft stainless steel column packed with 20% Carbowax 20M poly(ethylene glycol) on Gas Chrom Z support was used. Reaction products were determined quantitatively from comparison of component to internal standard peak height ratios with similar ratios determined from standard solutions which were prepared from distilled commercial samples of the expected reaction products. No major components other than the expected products were detected during the oxidations.

Results

Charge data, oxygen absorption data, and products found in the oxidation experiments are summarized in Table I.

Our product data were interpreted in terms of the following propagation reactions.

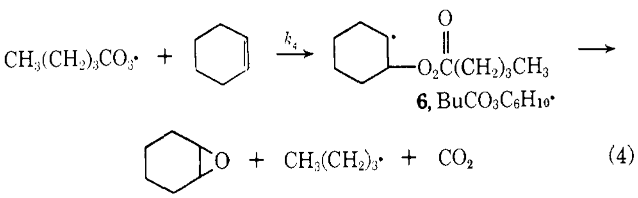


---

(16) D. E. Van Sickle, F. R. Mayo, and R. M. Arluck, *J. Amer. Chem. Soc.*, **87**, 4832 (1965).

(17) D. E. Van Sickle, D. G. Hendry, J. K. Castleman, and C. W. Gould, *J. Org. Chem.*, **36**, 3423 (1971).

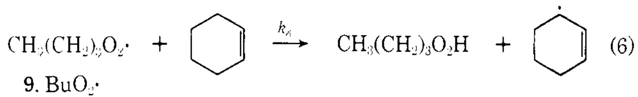
(18) R. D. Mair and A. J. Graupner, *Anal. Chem.*, **36**, 194 (1964); Hercules Method I was used.


6, $BuCO_3C_6H_{10}\cdot$

(4)

7, $c\text{-}C_6H_{10}O$ 8, $Bu\cdot$

$$CH_3(CH_2)_3CO_3\cdot + CH_3(CH_2)_3CHO \xrightarrow{k_5} CH_3(CH_2)_3CO_3H + CH_3(CH_2)_3CO\cdot \quad (5)$$

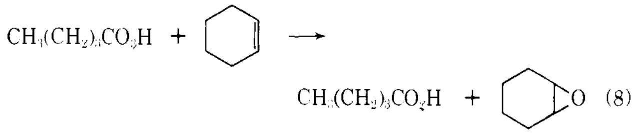

(6)

9. $BuO_2\cdot$

$$CH_3(CH_2)_3O_2\cdot + CH_3(CH_2)_3CHO \xrightarrow{k_7} CH_3(CH_2)_3O_2H + CH_3(CH_2)_3CO\cdot \quad (7)$$

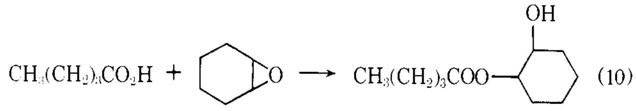
All alkyl and acyl radicals, except **6**, are assumed to be rapidly converted to the corresponding peroxy radicals by the oxygen present. To give a model tractable to analysis, addition reactions of both cyclohexenylperoxy and butylperoxy radicals to cyclohexene have been omitted. Errors of 5–10% in calculated rate constants may be generated by this approximation. Calculated kinetic chain lengths range from 240 upward based on a calculated[16] initiation rate of 7.2×10^{-6} M min^{-1} for 0.01 M initiator, so products from initiator fragments and termination reactions can be justifiably neglected.

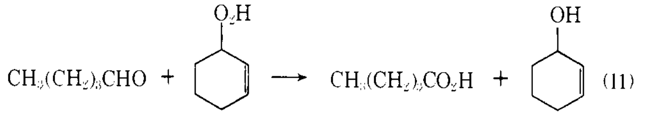
The following nonradical reactions were considered in treatment of the data.[6,19]


(8)

$$CH_3(CH_2)_3CO_3H + CH_3(CH_2)_3CHO \longrightarrow 2CH_3(CH_2)_3CO_2H \quad (9)$$

The following reactions were investigated and found to be unimportant at reaction conditions used in this study.


(10)


(11)

Reaction 10 was attempted by maintaining the reactants at normal oxidation temperature (60°) for 4 days. Examination of the final reaction mixture of reaction 10 by gas chromatography indicated that no reaction occurred. Reaction 11 was investigated by oxidizing cyclohexene at 60° and then adding valeraldehyde. The resulting mixture was analyzed for hydroperoxide and acid and then maintained at 60° without oxygen for 20 hr. No significant change was detected upon reanalysis.

To investigate the possibility that the valerylperoxy–cyclohexene adduct (**6**) might be scavenged by oxygen rather than undergo decarboxylation, as shown, reaction product from the cooxidation conducted at high oxygen pressure (run 53) was distilled to a head temperature of 50° at 0.1 mm of pressure. From a distillation charge of 15 g only 14 mg of residue was obtained; thus, the formation of any high molecular weight product similar to the "peroxide dimers" from simple olefin autoxidations[4] is not an important reaction.

A linear model for use in calculation of rate constant ratios was derived from expressions for the rates of formation of epoxide and peroxy acid taken from reactions 1 through 5.

$$\frac{d[BuCO_3H]}{dt} = k_3[BuCO_3\cdot][c\text{-}C_6H_{10}] + k_5[BuCO_3\cdot][BuCHO] \quad (12)$$

$$\frac{d[c\text{-}C_6H_{10}O]}{dt} = k_4[BuCO_3\cdot][c\text{-}C_6H_{10}] \quad (13)$$

Dividing (12) by (13) and simplifying

$$\frac{d[BuCO_3H]}{d[c\text{-}C_6H_{10}O]} = k_3/k_4 + k_5/k_4\frac{[BuCHO]}{[c\text{-}C_6H_{10}]} \quad (14)$$

A second linear model was similarly derived.

$$\frac{-d[BuCHO]}{d[c\text{-}C_6H_{10}O]} = \frac{k_3 + k_4}{k_4} + k_5/k_4\frac{[BuCHO]}{[c\text{-}C_6H_{10}]} \quad (15)$$

A nonlinear model which includes reactions 6 and 7 was also used in calculation of rate constant ratios. It was derived from the usual steady state assumption[20] for the radical intermediates **1**, **4**, and **9**. In terms of the butylperoxy radical (**9**), we obtained the following expressions for the valerylperoxy radical and cyclohexenylperoxy radical (**1**).

$$[BuCO_3\cdot] = \left(\frac{k_6[c\text{-}C_6H_{10}] + k_7[BuCHO]}{k_4[c\text{-}C_6H_{10}]}\right)[BuO_2\cdot] \quad (16)$$

$$[c\text{-}C_6H_9O_2\cdot] = \left(\frac{k_6(k_3 + k_4)[c\text{-}C_6H_{10}] + k_3k_7[BuCHO]}{k_2k_4[BuCHO]}\right)[BuO_2\cdot] \quad (17)$$

The equation for differential consumption of the reactants in the usual copolymerization[20] or cooxidation[21] form was, after substantial algebraic manipulation

$$\frac{-d[c\text{-}C_6H_{10}]}{-d[BuCHO]} = \frac{[c\text{-}C_6H_{10}]}{[BuCHO]}\left(\frac{1}{k_2(k_3 + k_4)[c\text{-}C_6H_{10}] + k_2k_5[BuCHO]}\right) \times \left(k_1k_3[c\text{-}C_6H_{10}] + k_2(k_3 + k_4)[BuCHO] + \frac{k_1k_4k_6[c\text{-}C_6H_{10}]^2 + k_2k_4k_6[BuCHO][c\text{-}C_6H_{10}]}{k_6[c\text{-}C_6H_{10}] + k_7[BuCHO]}\right) \quad (18)$$

Notice that where addition of valerylperoxy radical (**5**) to cyclohexene is taken from the mechanism, *i.e.*, $k_4 = 0$, expression 18 readily simplifies to

$$\frac{-d[c\text{-}C_6H_{10}]}{-d[BuCHO]} = \frac{[c\text{-}C_6H_{10}]}{[BuCHO]}\left(\frac{r_b[c\text{-}C_6H_{10}] + [BuCHO]}{r_a[BuCHO] + [c\text{-}C_6H_{10}]}\right) \quad (19)$$

---

(19) B. Phillips, F. C. Frostic, Jr., and P. S. Starcher, *J. Amer. Chem. Soc.*, **79**, 5982 (1957).

(20) C. Walling, "Free Radicals in Solution," Wiley, New York, N. Y., 1957, p 100.

(21) F. R. Mayo, M. G. Syz, T. Mill, and J. K. Castleman, *Advan. Chem. Ser.*, No. 75, 38 (1968).

Table II. Values for Solution of Equations

Run	mmol Δ[BuCHO][a]	Δ[c-C_6H_{10}][b]	Δ[c-$C_6H_{10}O$][c]	Δ[$CuCO_3H$]	Δ[BuCHO]/ Δ(c-C_6H_{10}]	Δ[BuCHO]/ Δ[c-$C_6H_{10}O$]	Δ[$BuCHO_3$]/ Δ(c-$C_6H_{10}O$]	[BuCHO]/ [c-C_6H_{10}]$_{av}$
31	3.17	11.38	1.97	1.20	0.30	1.74	0.74	0.037
43	3.09	11.56	1.75	1.34	0.27	1.76	0.76	0.038
39	5.23	10.94	2.91	2.32	0.48	1.81	0.80	0.074
26	6.89	9.91	3.84	3.05	0.69	1.80	0.80	0.120
41	6.73	9.85	3.65	3.08	0.69	1.85	0.84	0.119
37	9.37	10.56	4.54	4.83	0.89	2.06	1.06	0.180
33	10.15	8.88	4.46	5.69	1.14	2.27	1.28	0.269
51	12.69	9.31	5.27	7.42	1.36	2.41	1.41	0.409
53	8.58	9.81	4.00	4.58	0.88	2.14	1.14	0.179
56	9.61	12.09	4.97	4.64	0.80	1.94	0.93	0.178
57	9.44	10.77	4.95	4.44	0.87	1.90	0.91	0.179

[a] Δ[BuCHO] = [$BuCO_3H$] + [butyraldehyde] + [butyl alcohol]. [b] Δ[c-C_6H_{10}] = [c-$C_6H_{10}O$] + [cyclohexenol] + [cyclohexenone]. [c] Δ[c-$C_6H_{10}O$] = [butyraldehyde] + [butyl alcohol].

which is the usual form of the copolymerization or cooxidation equation with $r_b = k_1/k_2$ and $r_a = k_5/k_3$.

For computer fitting of (18) a reciprocal parameterized form was used

$$\frac{-d[\text{BuCHO}]}{-d[\text{c-C}_6\text{H}_{10}]} = \frac{[\text{BuCHO}]}{[\text{c-C}_6\text{H}_{10}]}(\alpha + \beta[\text{c-C}_6\text{H}_{10}] + [\text{BuCHO}]) \times \frac{[\text{c-C}_6\text{H}_{10}] + \epsilon[\text{BuCHO}]}{([\text{c-C}_6\text{H}_{10}] + \epsilon[\text{BuCHO}])[\beta\gamma[\text{c-C}_6\text{H}_{10}] + (\alpha + \beta)[\text{BuCHO}]] + \gamma\alpha[\text{c-C}_6\text{H}_{10}]^2 + \alpha[\text{BuCHO}][\text{c-C}_6\text{H}_{10}]} \quad (20)$$

where $\alpha = k_4/k_5$, $\beta = k_3/k_5$, $\gamma = k_1/k_2$, and $\epsilon = k_7/k_8$.

Values used in the solution of eq 14, 15, and 20 are presented in Table II.

Changes in concentration of **3**, **2**, and **7** were determined as indicated in Table II, footnotes *a–c*. The epoxide concentration in *c* includes only the epoxide formed in reaction 4. The sum of the concentrations of butyl alcohol and butyraldehyde is a measure of epoxide formed in reaction 4. The CO_2 yield should also equal the epoxide formed by radical addition, but the alcohol–aldehyde combination was believed to be more reliable. In these experiments CO_2 yields were usually less than butyl alcohol–butyraldehyde yields, especially with runs at high valeraldehyde feed concentrations. The butyl radical **8** formed in reaction 4 was scavenged by oxygen, and the butylperoxy radical abstracted a hydrogen from either substrate (cyclohexane or valeraldehyde) to give butyl hydroperoxide as the primary product. Apparently, a small amount of the butyl hydroperoxide was dehydrated to butyraldehyde, but most of this hydroperoxide was detected as butyl alcohol after the triphenylphosphine reduction. Peroxyvaleric acid concentration in Table II includes the total peroxy acid in the system: unreacted peroxyvaleric acid and peroxyvaleric acid consumed in nonradical reactions 8 and 9. The amount of unreacted peroxyvaleric acid, determined from the difference in total peroxide found iodometrically and total hydroperoxide (2-cyclohexen-1-ol + butyl alcohol) found by gas chromatography, was negligible and was ignored in this work. The amount of peroxyvaleric acid consumed in reaction 8 was equal to the difference in the total amount of epoxide and the amount of epoxide formed by radical addition [total epoxide − (butyl alcohol + butyraldehyde)]. The amount of peroxyvaleric acid consumed in reaction 9 was equal to one-half of the difference between the amount of total acid found in the reduced oxidation product and the amount of peroxyvaleric acid calculated to have been consumed in reaction 8.

Values in Table II were used to calculate rate constant ratios from linear expressions 14 and 15 and from nonlinear expression 20. Least-squares computer solution of expression 14 resulted in rate constant ratios of 0.655 (σ = 0.04) for k_3/k_4, 0.510 (σ = 0.07) for k_4/k_5, and 0.334 for k_3/k_5. Similar solution of (15) gave ratios of 0.659 (σ = 0.04) for k_3/k_4, 0.515 (σ = 0.07) for k_4/k_5, and 0.340 for k_3/k_5.

A computer program[22] for parameter fitting of nonlinear equations was applied to eq 20. If all four parameters of (20) were adjustable, usefully precise values could not be computed. However, when the ratio of β/α was fixed ($\beta = 0.66\alpha$) from the linear results, values of 0.38 (σ = 0.02) for $\alpha(k_4/k_5)$, 0.14 (σ = 0.13) for $\gamma(k_1/k_2)$, and 37.4 (σ = 113) for $\epsilon(k_7/k_6)$ were obtained. There are indications from an alternate calculation of γ that its value is more precisely known than the computer calculation of its standard deviation would indicate. If (20) is written in inverse form

$$\frac{d[\text{c-C}_6\text{H}_{10}]}{d[\text{BuCHO}]} = \frac{[\text{c-C}_6\text{H}_{10}]}{[\text{BuCHO}]}\left(\frac{1}{(\alpha + \beta)[\text{c-C}_6\text{H}_{10}] + [\text{BuCHO}]}\right) \times \left(\beta\gamma[\text{c-C}_6\text{H}_{10}] + (\alpha + \beta)[\text{BuCHO}] + \frac{\alpha\gamma[\text{BuCHO}]^2 + \alpha[\text{BuCHO}][\text{c-C}_6\text{H}_{10}]}{[\text{c-C}_6\text{H}_{10}] + \epsilon[\text{BuCHO}]}\right)$$

one notes that for large [c-C_6H_{10}]/[BuCHO] ratios, *i.e.*, [c-C_6H_{10}]/[BuCHO] $\rightarrow \infty$, d[c-C_6H_{10}]/d[BuCHO] = γ[c-C_6H_{10}]/[BuCHO]. Apparently, all of the experiments were run in the upper limit range of [c-C_6H_{10}]/[BuCHO], for a plot of our Δ[c-C_6H_{20}]/Δ[BuCHO] values *vs.* [c-C_6H_{10}]/[BuCHO] gives a very good straight line (correlation coefficient of 0.99) whose slope is 0.114 (σ = 0.006). The agreement with the value of 0.14 from the computer fitting of (20) is excellent.

The significance of the parameter ϵ has not yet been

---

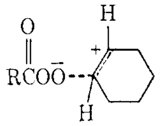
[22] Y. Bard, "Nonlinear Parameter Estimation and Programming," New York Scientific Center Report 360D-13.6.003, IBM, December, 1967.

determined. By taking the values of the parameters α, β, and γ (0.51, 0.34, and 0.12, respectively), one can calculate a value of ϵ for each of the first eight runs of Table II. This was done and, while reasonable ϵ values of 14.7 and 13.3 were calculated for runs 43 and 39, the ϵ values calculated then ascend for the higher valeraldehyde concentration runs to 55.6 (run 37) and then descend to large negative numbers. Evidently, at "high" valeraldehyde concentrations other reactions, which we have not recognized in our seven-reaction model and which are certainly not manifested by the appearance of new products, contribute to the formation and/or disappearance of the butyl radical.

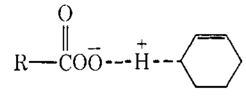
Discussion

The rate constant ratio (k_3/k_4) determined for the addition–abstraction reactions of valerylperoxy radicals with cyclohexene indicates that addition predominates by a factor of 1.5. Previous work on the liquid phase oxidation of cyclic alkenes has shown that the abstraction–addition ratio for attack of cyclohexenylperoxy radical on cyclohexene is 22:1.[4]

The reasons for the preference of acylperoxy radicals to add to double bonds rather than to abstract allylic hydrogens are not known. However, one possible reason for the addition preference is that the highly electrophilic[23] character of the acylperoxy radical imparts a large amount of polar character on the transition state. Evidently, the addition mode allows a better stabilization of the partial positive charge induced on the substrate

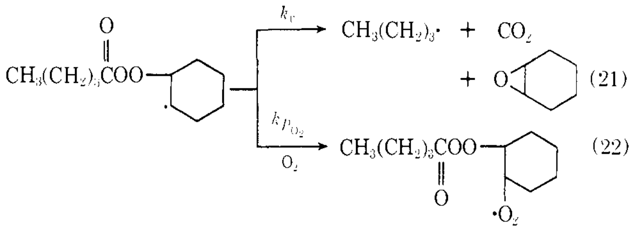


than is obtained in the transition state for the abstraction mode



Another interesting aspect of the key reaction 4 is its relative insensitivity to oxygen concentration. Although most runs were made at ~12 psia of oxygen pressure, one (run 53) at 75 psia showed a scarcely diminished yield of epoxide. That the radical adduct (**6**), unlike normal alkyl radicals,[24] is not readily scavenged by oxygen suggests that **6** is never fully formed before it enters into a "concerted" decomposition or that its decomposition is very rapid and comparable to bimolecular collision frequency.

If the competition between decomposition and oxygen scavenging is as shown in reactions 21 and 22, a value of $k_{P_{O_2}}/k_r$ can be estimated by methods previously described.[25]



First, the amount of cyclohexene reacting only with valerylperoxy radicals is calculated by adding the epoxide formed from radical addition to the peroxyvaleric acid produced by the abstraction reaction ([total valeric acid]k_3[c-C_6H_{10}]/(k_3[c-C_6H_{10}] + k_5[BuCHO)]. The yield of epoxide (d[c-C_6H_{10}O]/−d[c-C_6H_{10}]), Y, is then calculated, and it has been shown to be related to the concentration of oxygen in solution by an equation of the form

$$Y = \frac{1}{A + B[O_2]} \tag{23}$$

B is still $k_{P_{O_2}}/k_r f_a$, but A is now $1/f_a$ instead of $1 + 1/f_a$ as given previously.[25] The different identity of A arises because only attack on the substrate (cyclohexene) by valerylperoxy radicals is being considered here. The quantity f_a is the fraction of valerylperoxy radicals which react by addition: $k_4/(k_3 + k_4) = 0.60$. By using the data of runs 37 and 53, taking the concentration of oxygen to be 0.01 M atm^{-1}, and solving the pair of equations simultaneously for B, we find $k_{P_{O_2}}/k_r$ = 0.8. The answer is necessarily crude since so little diminution of epoxide yield was effected by the higher pressure, but the value for $k_{P_{O_2}}/k_r$ is the lowest yet found. For the cycloheptenylperoxy radical–cycloheptene adduct, a value of 34 was determined.[24]

The relative reactivities of the valerylperoxy radical (**4**) and the cyclohexenylperoxy radical (**1**) toward the two substrates **2** and **3** are available from our data. Thus, by the usual convention, $r_a = k_5/(k_3 + k_4)$ = 1.18 when reaction of the valerylperoxy radical with cyclohexene by both modes (addition and abstraction) is considered or $r_a = k_5/k_3 = 2.94$ when only abstraction is considered. The value for r_b is simply k_1/k_2 (or γ) = 0.14. A criterion for "correctness" of $r_a r_b$ values is that they should equal unity or at least be no lower than 0.5.[21] Zaikov, Howard, and Ingold[23] found this to be so in the cooxidation of various aldehydes with 1,4-cyclohexadiene, a particularly reactive alicyclic hydrocarbon which reacts by abstraction but which results in $HO_2\cdot$ as the chain carrying radical. The $r_a r_b$ values in our case are 0.16 and 0.41 (abstraction only). If the problem lies in the determination of k_1/k_2 where the computer output (parameter fitting of eq 20) indicates a standard deviation of 0.13, the value of k_1/k_2 could be as high as 0.27, and the $r_a r_b$ (abstraction only) value becomes 0.80, apparently within acceptable range. However, when both modes of reaction are taken, $r_a r_b$ is still less than 0.5. It therefore appears that the criterion of $r_a r_b = 1$ for cooxidations may not be applicable to systems in which there is significant propagation by acylperoxy radical addition to olefins. The extraordinarily high[23] absolute reactivity of acylperoxy radicals in abstraction reactions suggests they will show exception to simple correlation rules.

---

(23) G. E. Zaikov, J. A. Howard, and K. U. Ingold, *Can. J. Chem.*, 47, 3017 (1969).

(24) S. W. Benson, *J. Amer. Chem. Soc.*, **87**, 972 (1965).

(25) D. E. Van Sickle, F. R. Mayo, E. S. Gould, and R. M. Arluck, *J. Amer. Chem. Soc.*, **89**, 977 (1967).