

Oxidations of Acyclic Alkenes¹

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Abstract: Rates and products of oxidation have been determined for ethylene, propylene, 1-butene, 2-butene, isobutylene, trimethylethylene, 3-methyl-1-butene, tetramethylethylene, 2-methyl-1-pentene, 1-hexene, *t*-butylethylene, neopentylethylene, 1-hexyne, and 3-hexyne at 50–100°. The assignment of products, which are mostly primary, to the addition and abstraction mechanisms of oxidation is discussed, with special attention to the nature of the nonvolatile residues. Ethylene and *t*-butylethylene react only by the addition mechanism, isobutylene 80% by that mechanism. 3-Methyl-1-butene and both alkynes react about 90% by the abstraction mechanism. With all the other alkenes listed, the addition–abstraction competition is balanced between 1:2 and 2:1. Rates of reaction by the addition mechanism correlate well with the calculated (electronic) excitation energies of the alkenes. Rates of reaction by the abstraction mechanism cover a wider range and are affected enough by inductive and steric effects and by the numbers of reactive hydrogen atoms that no quantitative correlation with structure is obvious. Because of their high vapor pressures, ethylene and propylene were oxidized in benzene solutions. They are unreactive and gave large proportions of residues. The oxidation of *t*-butylethylene gave 34% yield of *t*-butyl alcohol. The oxidation of neopentylethylene was the most complicated and gave a poor material balance. The 1- and 3-hexynes oxidized 3–5 times as fast as the corresponding hexenes, but almost entirely by the abstraction mechanism.

We have described previously the rates and primary products of oxidation of several cyclic alkenes at 50–80° in terms of the addition and hydrogen-abstraction mechanisms of oxidation.^{2a} The present paper extends that study to 12 acyclic alkenes and to two alkynes, all of two to seven carbon atoms. The following paper^{2b} describes some effects of oxygen pressure, temperature, solvents, and conversion on oxidations of some of these alkenes and relates our work to some of the recent literature.

Experimental Section

The oxidations of ethylene and propylene were carried out independently by Dr. M. G. Syz by different procedures described in section 4.

1. Materials. The benzene solvent used for some runs on volatile olefins was untreated Matheson Coleman and Bell "chromato quality" grade. Isobutylene and 1- and 2-butene were Phillips research grade and were distilled from degassed alumina^{2a} on the vacuum line just prior to use. 3-Methyl-1-butene and trimethylethylene were obtained from Columbia Chemical Co. The trimethylethylene was distilled through a small column and passed over neutral alumina just before use. The 3-methyl-1-butene was distilled on and off alumina in a vacuum line. Glpc traces of both olefins showed the purities to be better than 99%. Since commercial tetramethylethylene contained ~5% of an unidentified contaminant, we synthesized the material by a National Bureau of Standards procedure.³ Glpc analysis showed our material to be 97.9% 2,3-dimethyl-2-butene and 1.8% 2,3-dimethyl-1-butene. 1-Hexene was Matheson Coleman and Bell "99%" grade and was passed over alumina before use. The *t*-butylethylene, a complimentary sample from Sinclair Petrochemicals, was distilled before use but not passed over alumina. Neopentylethylene was Columbia Chemical Co. material. Both the *t*-butylethylene and neopentylethylene appeared to be homogeneous (>99%) by glpc. 2,2'-Azobis(2-methylpropionitrile) (ABN) was Eastman White Label grade, recrystallized from acetone–methanol. 1,1'-Azobis(cyclohexane-1-carbonitrile) (ABC) was synthesized⁴ or in some runs was a recrystallized product of the Koch-Light Co., Ltd.

2. Oxidation Procedure. C₅, C₆, and C₇ hydrocarbons were oxidized without solvent. Solutions of ABN or ABC (usually 0.01 M) were made in volumetric flasks and then transferred to the oxidation vessels. An exception was 3-methyl-1-butene which was distilled directly into the reaction bulb from alumina. The ABN was previously introduced into the bulb in benzene as solvent, later evaporated under vacuum. The C₄ alkenes were oxidized as benzene solutions. The benzene was added to the bulb by hypodermic syringe and the alkene was then condensed from the vacuum line.

Our apparatus and its operation have been described previously.^{2a} Rates were measured by decreases in oxygen pressure in a fixed volume system. The amount of oxygen absorbed was determined both by the gain in weight of the reaction bulb and by the total pressure drop in the oxygen reservoir. For C₅, C₆, and C₇ hydrocarbons, the agreement was usually within 5%. For butenes, evaporation losses permitted use only of pressure changes. When there was little fragmentation of the olefin and little formation of aldehyde, any formation of CO₂, CO, and H₂ was neglected. When considerable fragmentation occurred with *t*-butyl- and neopentylethylenes, the final gases were sampled and corrections applied.

3. Analyses. a. Distillations. After oxidations of the butenes in benzene solution, the unreacted butene was distilled away at atmospheric pressure and a liquid temperature up to 70° through a 30-cm Vigreux column and with a Dry Ice cooled dewar head to maintain reflux. The remaining benzene solution of products was titrated⁵ for hydroperoxide, then processed as the neat hydrocarbons were (see below). The recovered olefin was analyzed by glpc for the small quantities of products which distilled with it.

The oxidates of C₅, C₆, and C₇ hydrocarbons, after titration for hydroperoxide, were distilled at reduced pressure (40 mm) so that most of the unreacted hydrocarbon could be removed at room temperature. The hydrocarbon distillate (A) was saved for analysis. A weighed portion of the undistilled portion was transferred to a small one-piece Claisen distillation rig where materials (B) distilling up to 70° (liquid temperature, 0.1 mm) were collected in a receiver cooled in liquid nitrogen and separated from the residue (C). After the distillation, the condenser was washed down with small portions of benzene which were combined with the distillate (B). The weighed residue (C) was saved, usually as an ethanol solution.

b. Volatile Fractions. The butenes recovered were free of hydroperoxide and could be analyzed directly by glpc. Recovered C₅ to C₇ hydrocarbons as well as benzene solutions (A) usually contained small amounts of hydroperoxide which were reduced with a slight excess of triphenylphosphine⁶ before examination by glpc. After titration of an aliquot for peroxide, the remaining distillate (B) was treated with a small excess of solid triphenylphosphine at 0° prior to examination by glpc.

(1) Research sponsored by AFOSR (SRC)-OAR, U. S. A. F. Contract No. AF49 (638)-1102.

(2) (a) D. E. Van Sickle, F. R. Mayo, and R. M. Arluck, *J. Am. Chem. Soc.*, **87**, 4824 (1965); (b) D. E. Van Sickle, F. R. Mayo, E. S. Gould, and R. M. Arluck, *ibid.*, **89**, 977 (1967).

(3) F. L. Howard, T. W. Means, A. Fookson, P. Pomerantz, and D. B. Brooks, *J. Res. Natl. Bur. Std.*, **38**, 365 (1947).

(4) C. G. Overberger, M. T. O'Shaughnessy, and H. Shalit, *J. Am. Chem. Soc.*, **71**, 2661 (1949).

(5) J. P. Wibaut, H. B. Van Leeuwen, and B. van der Wal, *Rec. Trav. Chim.*, **73**, 1033 (1954).

(6) L. Horner and W. Jurgleit, *Ann. Chem.*, **591**, 138 (1955).

Most of the glpc work was done on a Wilkins A90-P instrument using a 4-m Carbowax 20 M column. "W-1" filaments were used in the detector. A few analyses were done with a 5-ft didecyl phthalate column. The glpc peak areas were taken to be proportional to weight per cent. To check this assumption a known mixture was prepared and analyzed (glpc results in parentheses): 2,3-epoxybutane, 3.12% (3.23); 1,2-epoxybutane, 3.54% (3.56); benzene, 86.57% (85.90); crotonaldehyde, 3.54% (3.79); and 2-buten-1-ol, 3.24% (3.51).

Identification of most of the volatile products was made by internal comparison of retention times with authentic samples. In a few cases, product from the glpc effluent was trapped and the infrared spectrum compared with an authentic sample. In the few instances where authentic samples of expected products were not readily accessible, identification was made by nmr spectra of trapped glpc effluent (footnote *gg*, Table I). In three cases, product identity was surmised by analogy with other olefin oxidations and the relative retention times of the glpc peaks (footnote *m*, Table I). In all cases, the structure of the volatile hydroperoxides was assumed to correspond to the allylic alcohols found in the reduced distillate.

c. Residues. The ethanol solutions of the residues were titrated for free hydroperoxides and, with the exception of 3-methyl-1-butene, which has a nearly theoretical titer for "peroxide dimer," a solvent-free sample of the residue was analyzed for carbon and hydrogen. Further work on isobutylene oxidation residues is described under Investigation of Isobutylene Residues.

4. Ethylene and Propylene. Because of their low boiling points and low reactivities in oxidation, ethylene and propylene were oxidized in sealed tubes in benzene as solvent. Each experiment employed a glass reaction vessel equipped with a break-seal and two capillary inlets. The vessel was connected to the vacuum line and the solution of benzene and initiator (0.10 *M*) was added through one of the capillaries and the alkene and oxygen through the other. The molar ratio of benzene to alkene was close to 1. During the reaction the vessel was shaken in an oil or water bath. Afterward, the vessel was again attached to the vacuum line through the break-seal and the contents were analyzed for remaining oxygen, nitrogen from the initiator, and carbon monoxide. Most of the unreacted hydrocarbon was distilled away from the reaction mixture at -78° (with one thawing of the benzene solution while it was separated from the pump). The benzene solution was then distilled up to 50° (0.1 mm), thus removing all products having a boiling point below 240° (1 atm). A sample of the distillate was titrated for hydroperoxide,⁵ and the other products were determined by glpc. The low-boiling products from propylene were analyzed with a Carbowax 20 M column at 50° using *t*-butyl alcohol as internal standard, and the products from ethylene on a Hallcomid column at 40° . In each case the filament detector described in section 3b was used. The high-boiling products were analyzed at 140° with acetophenone as standard. Peak areas were assumed to be proportional to per cents by weight, an assumption confirmed by tests with propylene oxide and propylene glycol. The residue from the original distillation was analyzed for C, H, and N. The results are expressed as formulas containing 1, 2, or 3 carbon atoms; no molecular weights were determined.

Average oxygen pressure was varied by the amount of oxygen added and the size of the reaction tube.

5. Investigation of Isobutylene Residues. In order to obtain enough nonvolatile products for investigation, oxidations of isobutylene were carried out in a glass-lined Aminco stainless steel pressure vessel. One oxidation was carried out with 3.0 *M* isobutylene in benzene at 90° with 0.01 *M* ABC as initiator. In the following account of this experiment, results of a nearly parallel experiment with 0.01 *M* ABC and without solvent at 80° are given in parentheses.

About 3% (5%) of the isobutylene charged was recovered as nonvolatile residue after 24 (26) hr with 100–150 psia of oxygen. Assuming C_4 units, the residues analyzed for $C_4H_{7.03}O_{1.79}$ ($C_4H_{7.70}O_{2.16}$) (compare with $C_4H_{6.98}O_{1.60}$, footnote *j*, Table I). The principal infrared absorption bands were at 2.95, 3.4, 5.8, 6.8, and 7.3μ . A shoulder at 6.23μ on the main carbonyl band appeared in the benzene solution product (but not in the other).

This residue was hydrogenated with fully active 5% palladium-on-charcoal catalyst in ethyl acetate as solvent. The residue absorbed 1.36 (1.80) mmoles of H_2/g . When no more hydrogen was absorbed, the catalyst was separated, and the solution of hydrogenated residue was distilled up to a pot temperature of 80° (0.1 mm). As a result, 41% (57%) of the residue was found to be volatile. Glpc analysis of the distillate showed isobutylene glycol and isobutyraldehyde to be the major products in the ratio 1.77 (2.11). About

20% of isobutane and unidentified volatiles were nearly sufficient to balance the weight loss of starting residues. The balance of the analysis is disturbed in part by the formation of isobutane, detected in the glpc trace, which presumably was partially lost in manipulating the hydrogenated solution.

The nonvolatile product, 59 (43) wt % of the starting material, analyzed for $C_4H_{6.78}O_{1.50}$ ($C_4H_{7.59}O_{1.90}$). The infrared spectrum was almost unchanged from the starting material. The nmr spectrum showed strong methyl absorption at δ 1 and, presumably, methylene with neighboring oxygen absorption centered around δ 4. A small signal for vinyl hydrogens at δ 5 was also present.

This hydrogen-refractory residue (333 mg) was then heated for 12 hr at 70° in a sealed tube with 5.0 g of anhydrous hydrogen iodide. Only 0.152 mmole of permanent gas (61% CO , 14.3% H_2 , 16.3% N_2 , 7.7% CH_4) was formed, and 0.53 mmole of light boilers (mostly butane, butene, and CO_2) could be isolated. The residue in the tube was extracted with chloroform and the iodine removed from the chloroform by extraction with KI solution. No volatile materials could be found in this chloroform solution and evaporation of the solvents yielded only 185 mg of black resinous material, $C_4H_{6.81}O_{1.30}$.

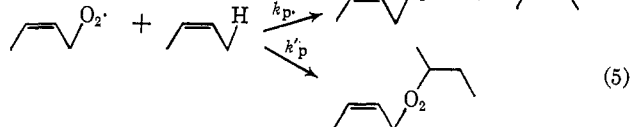
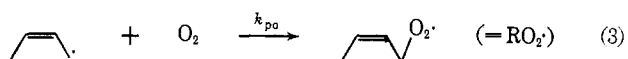
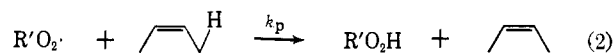
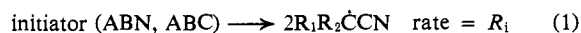
Rate and Product Data

The results of analyses of oxidations of ten alkenes and two alkynes are given in Table I. The average partial pressures of oxygen listed (\bar{P}_{O_2}) were calculated from the total gauge pressure, the initial amount of nitrogen (air) in the reaction bulb, the nitrogen produced by ABN (or ABC) decomposition, and the vapor pressures⁷ of the hydrocarbons (or their benzene solutions) at the reaction temperature. For *t*-butylethylene and neopentylethylene, the permanent gases formed (H_2 and CO) were also taken into account. If other oxidations produced significant amounts of hydrogen or carbon monoxide, the average oxygen pressures were lower than stated values.

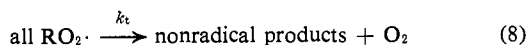
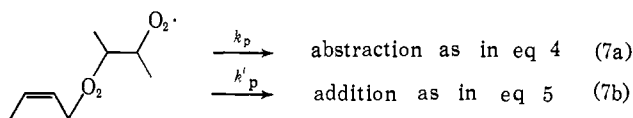
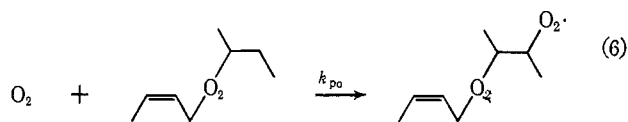
Tables II and III show our results with ethylene and propylene in benzene solution, using the different techniques described in Experimental Section 4. Table IV summarizes rate data of all the oxidations. Table V summarizes product data of the alkene oxidations and assigns contributions of the addition and abstraction mechanisms to the over-all composite rate constants.

Definitions and Conventions

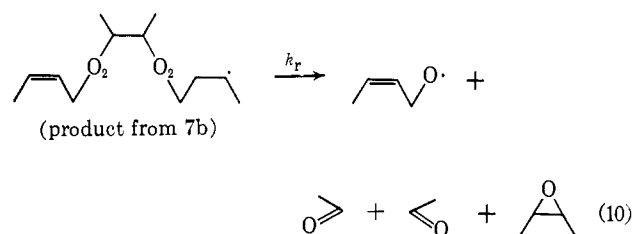
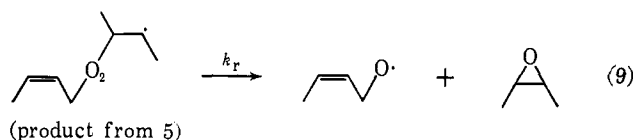
Our oxidations are discussed in terms of the same equations and terminology we used for the cyclic alkenes.^{2a} 2-Butene is used as example without any implications for stereochemistry.



(7) D. R. Stull, *Ind. Eng. Chem.*, **39**, 517 (1947).



To account for epoxides and double-bond cleavage products (carbonyl compounds), additional reactions must be postulated



The alkoxy radicals formed by eq 9 and 10 are expected to react like peroxy radicals in eq 4 and 5 to give alcohols and ethers.

If reactions 4, 5, and 7 are rate determining, then the over-all rate of oxidation is

$$-d\text{O}_2/dt = R_{\text{O}_2} = (R_i/2k_t)^{1/2}(k_p + k'_p)[\text{alkene}] \quad (11)$$

where R_i is the rate of initiation. Rates of initiation are calculated from

$$R_i = 2ek_d[\text{ABN}] \text{ (or } [\text{ABC}]) \quad (12)$$

Values of k_d for the decomposition of ABN⁸ were taken to be 0.00842/hr (50°), 0.0358/hr (60°), and 0.144/hr (70°), and for ABC⁹ to be 0.0299/hr (80°) and 0.119/hr (90°); the value of e is taken to be 0.60⁹ for both ABN⁸ and ABC.⁹

Discussion

Some recent literature on oxidations of acyclic alkenes is discussed in an accompanying report.^{2b}

1. Primary and Secondary Addition and Abstraction Products. Except in the oxidations of *t*-butylethylene and neopentylethylene, the volatile products of the acyclic olefin oxidations are mostly the primary ones of the equations in the Definitions and Conventions section, with small amounts of secondary products. The volatile hydroperoxides, epoxides, carbonyl compounds from cleavage at C=C bonds, and polyperoxide residues are primary products of the chain reaction. Readily identified as secondary products are α,β -unsaturated carbonyl compounds (when they arise by dehydration of hydroperoxides, not when they arise

from chain termination), glycols and glycol esters, acids, and part of the nonvolatile residues. Some epoxide might also arise by intervention of aldehydes; further oxidation of aldehydes^{2b} leads to acylperoxy radicals which might substitute for RO₂· in reaction 9, or to peracids which epoxidize alkenes by nonradical reactions. These reactions are unimportant at the low conversions which we used. Alkoxy radicals leading to alcohols and ketones may also be formed by non-terminating interactions of tertiary peroxy radicals. Epoxides, glycols and their esters, cleavage products, and polyperoxides and polyethers are clearly associated with the addition mechanism. Other products, including the terminal HO and HO₂ groups in polyperoxides, are associated with the abstraction mechanism. In several experiments, more epoxide than alcohol plus ether was found (see reaction 9). These differences are discussed in the accompanying paper.^{2b}

2. Nonvolatile Products. Our calculations assume that all of our oxidation residues are like those obtained in the oxidation of cyclic olefins, except that trimers as well as dimers of C_nH_{2n}O₂ units are possible. The assignment of residue to addition and abstraction mechanisms in Table V allots the millimoles of titratable peroxide groups to abstraction and the remainder of the C_nH_{2n}O units to addition. Two errors cause the addition assignment to be too high. To the extent that residue polymers are terminated by OH instead of O₂H, the fraction of abstraction is underestimated. To the extent that the residue includes polymerized α,β -unsaturated carbonyl compounds, the allylic hydroperoxides formed are wrongly assigned to addition rather than abstraction. Our results below with isobutylene residues (Experimental Section 5) suggests that the latter error is minor, even in an extreme case.

Since both the liquid-phase (Table I) and gas-phase^{10a} oxidations of isobutylene gave so much nonvolatile residue, an effort was made to determine by mild and strong reductions the nature of the building blocks in these products (Experimental Section 5). About 70% of two of these residues was thus converted into isobutylene glycol, isobutyraldehyde, isobutane (maybe isobutylene), and small proportions of lighter hydrocarbons. The remainder resisted reduction by anhydrous hydrogen iodide at 70°. We conclude that the original residue contained units corresponding mostly to polyperoxides of isobutylene (and the corresponding polyethers), to condensation and polymerization products of saturated and unsaturated aldehyde, and to oxidation products of all such units. If we count methacrolein as a product of the abstraction mechanism and isobutyraldehyde as a product of the addition mechanism (perhaps *via* isobutylene oxide), and about 20% of the polyperoxide and polyether units as terminal HO or HO₂ groups associated with the abstraction mechanism, then 70% of the residue arose from the addition mechanism.

3. Rate Constants for Addition, $k_p'/(2k_t)^{1/2}$. In this and the following section 4, we consider the effects of alkene structure on $k_p'/(2k_t)^{1/2}$ and on $k_p/(2k_t)^{1/2}$. Since we have not separated the propagation and termination reactions, we must assume that the effects of structure on $(2k_t)^{1/2}$ are small compared with their

(8) D. E. Van Sickle, F. R. Mayo, and R. M. Arluck, *J. Am. Chem. Soc.*, **87**, 4832 (1965), discuss the choice of k_d and e for ABN.

(9) C. S. Wu, G. Hammond, and J. Wright, *ibid.*, **82**, 5386 (1960).

(10) (a) P. S. Fredricks and F. R. Mayo, unpublished work. (b) J. A. Howard and K. U. Ingold, *Can. J. Chem.*, in press. We appreciate the opportunity to consider and discuss these results before publication.

Table I. Initiated Oxidations of Acyclic Alkenes and Alkynes at 50–90°


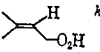






	Product	Amount, mmoles	Alkene equiv, mmoles	O ₂ equiv, mmoles	
360.8 mmoles of 1-butene in 59.01 g of benzene, 0.0093 M in ABN, absorbed 12.6 mmoles of O ₂ in 1462 min at 70° and $\bar{P}_{O_2} = 30$ psia (analytical sample corresponds to 12.5 mmoles of O ₂)	Volatile RO ₂ H ^a	6.62	6.62	6.62	
	Crotonaldehyde ^b	0.54	0.54	0.54 ^c	
	1,2-Epoxybutane	0.60	0.60	0.30	
	1-Butene glycol and monoformate	0.49 ^d	~0.49	~0.49	
	EtCHO ^e	0.17	0.17	0.17	
	Unknown volatiles	0.56	0.56	0.56	
	Residue ^f	2.81	2.81	3.32	
	Acetone (from ABN)	0.78	0.00	0.39	
	Total		11.8	12.4	
	323.8 mmoles of <i>trans</i> -2-butene in 60.28 g of benzene solution, 0.0094 M in ABN, absorbed 15.3 mmoles of O ₂ in 1603 min at 70° and $\bar{P}_{O_2} = 32$ psia (analytical sample corresponds to 15.2 mmoles of O ₂)	Volatile RO ₂ H ^a	3.46	3.46	3.46
2,3-Expoxybutane		2.31	2.31	1.16	
Butane-2,3-diol		0.80	0.80	0.80	
Butane-2,3-diol monoacetate		0.23	0.34	0.46	
Acetaldehyde		3.27	1.64	1.64	
Unknown volatiles ^g		1.62	1.62	1.62	
Residue ^h		4.99	4.99	5.41	
Acetone (from ABN) (50% theor)		1.07	0.0	0.53	
Total			15.2	15.0	
392.0 mmoles of isobutylene in 58.44 g of benzene solution, 0.0122 M in ABC, absorbed 11.9 mmoles of O ₂ in 1578 min at 80° and $\bar{P}_{O_2} = 32$ psia (analytical sample corresponds to 11.7 mmoles of O ₂)		Volatile RO ₂ H ⁱ	0.39	0.39	0.39
	Methacrolein	1.57	1.57	1.57 ^c	
	Isobutylene oxide	3.39	3.39	1.70	
	Isobutylene glycol	0.25	0.25	0.12	
	Isobutylene glycol monoformate	0.04	0.04	0.03	
	Acetone ^e	2.82	2.82	2.82	
	Unknown volatiles	0.58	0.58	0.58	
	Residue ^j	6.19	6.19	4.96	
	Total		15.2	12.2	
	454.7 mmoles of 3-methyl-1-butene, 0.0090 M in ABN, absorbed 12.9 mmoles of O ₂ in 465 min at 70° and $\bar{P}_{O_2} = 21$ psia (analytical sample corresponds to 12.8 mmoles of O ₂)	 +  ^k	10.75	10.75	10.75
Alcohols ^l		2.07 ^k	2.07	1.03	
 ^m		0.28	0.28	0.28 ^c	
		0.13	0.13	0.06	
Unknown volatiles		0.16	0.16	0.16	
Residue ⁿ		0.68	1.36	1.36	
Acetone (from ABN)		0.71	0.00	0.35	
Total			14.7	14.0	
465.0 mmoles of trimethyl ethylene, 0.00939 M in ABN, absorbed 21.3 mmoles of O ₂ in 785 min at 60° and $\bar{P}_{O_2} = 35$ psia (analytical sample corresponds to 18.3 mmoles of O ₂)		Primary RO ₂ H ^o }  	3.74	3.74	3.74
		Alcohols ^l	0.63 ^o	0.63	0.32
		0.23	0.23	0.23 ^c	
		1.94	1.94	0.97	
	AcH	1.28	<i>p</i>	<i>p</i>	
	Acetone	2.08	1.75 ^o	1.91 ^p	
	Unknown volatiles (4)	1.54	1.54	1.54	
	Residue ^q	9.45	9.45	10.30	
	Total		19.3	18.9	

Table I (Continued)






















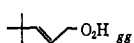











	Product	Amount, mmoles	Alkene equiv, mmoles	O ₂ equiv, mmoles	
413.8 mmoles of tetramethylethylene, 0.0096 M in ABN, absorbed 20.9 mmoles of O ₂ in 333 min at 50° and \bar{P}_{O_2} = 59 psia (analytical sample corresponds to 19.0 mmoles of O ₂)	 + 	8.57	8.57	8.57	
	Alcohol ⁱ	0.58 ^a	0.58	0.29	
		3.06	3.06	1.53	
		0.13	0.13	0.13	
	Acetone	4.31	2.16	2.16	
	Unknown volatiles (4) Residue ^a	0.84 4.32	0.84 4.32	0.84 4.88	
	Total		19.7	18.4	
384.7 mmoles of 2-methyl-1-pentene, 0.00955 M in ABN, absorbed 15.09 mmoles of O ₂ in 864 min at 70° and \bar{P}_{O_2} = 47 psia (analytical sample corresponds to 13.5 mmoles of O ₂)	 + 	2.17	2.17	2.17	
	Alcohol ⁱ	1.19 ^a	1.19	0.60	
		1.33	1.33	1.33 ^c	
		0.40	0.40	0.40 ^c	
		0.01	0.01	0.01 ^c	
		1.38	1.38	0.69	
		1.73	1.73	1.73 ^e	
	Residue ^u Acetone (from ABN)	5.06 0.12	5.06 0.00	6.33 0.12	
		Total		13.3	13.4
	383.8 mmoles of 1-hexene, 0.00892 M in ABC, absorbed 18.1 mmoles of O ₂ in 753 min at 90° and \bar{P}_{O_2} = 40 psia (analytical sample corresponds to 15.0 mmoles of O ₂)	 + 	4.66	4.66	4.66
Alcohol ⁱ		0.59 ^a	0.59	0.30	
		0.75	0.73	0.75 ^c	
		0.73	0.75	0.73 ^c	
		0.86	0.86	0.43	
		0.30	0.30	0.30 ^e	
Unknown volatiles (2) Residue ^w		0.12 5.87	0.12 5.87	0.12 6.96	
	Total		13.9	14.3	
759.5 mmoles of <i>t</i> -butylethylene, 0.0090 M in ABC, absorbed 14.1 mmoles of O ₂ in 1372 min at 90° and \bar{P}_{O_2} = 24 psia (analytical sample corresponds to 12.8 mmoles of O ₂)		0.60	0.60	0.60 ^e	
		3.23	3.23	1.61	
		3.35	3.35	5.02 ^z	
	Unknown volatiles (5) Residue ^v	0.49 2.06	0.49 2.06	0.49 2.04	
	Cyclohexanone (from ABC)	0.78	0.00	0.39	
		Total		9.7	10.2

Table I (Continued)

	Product	Amount, mmoles	Alkene equiv, mmoles	O ₂ equiv, mmoles
342.6 mmoles of neopentylethylene, 0.0122 M in ABC, absorbed 14.6 mmoles of O ₂ in 1320 min at 90° and \bar{P}_{O_2} = 31 psia (analytical sample corresponds to 12.5 mmoles of O ₂)	 + 	2.30	2.30	2.30
	Alcohol ^l	0.14 ^z	0.14	0.07
		0.14	0.14	0.14 ^c
		0.36	0.36	0.36
		0.64	0.64 ^{aa}	0.64 ^{aa}
		0.39	aa,bb	aa,bb
	Acetone	0.46	0.46 ^{cc}	0.69 ^{cc}
		2.35	2.35	1.18
		0.09	0.09	0.09
	Unidentified (5)	0.35	0.35	0.35
	Residue ^{dd}	3.04	3.04	2.23
Cyclohexanone (from ABC)	0.23	0.00	0.12	
Total			10.4	9.0
429.1 mmoles of 1-hexyne, 0.00095 M in ABN, absorbed 19.0 mmoles of O ₂ in 504 min at 70° and \bar{P}_{O_2} = 58 psia (analytical sample corresponds to 16.2 mmoles of O ₂)		2.80	2.80	2.80
		2.33	2.33	1.17
	Unknown volatiles (9)	3.16	3.16	3.16
	CO ₂	0.60	...	0.60
	Residue ^{ee}	3.30	3.30	3.43
Total			11.6	11.2
433 mmoles of 3-hexyne, 0.0094 M in ABN, absorbed 20.2 mmoles of O ₂ in 97 min at 60° and \bar{P}_{O_2} = 50 psia (analytical sample corresponds to 18.5 mmoles of O ₂)		12.39	12.39	12.39
		2.20	2.20	1.10
		1.89	1.89	1.89 ^c
	Unknown volatiles (5)	1.74	1.74	1.74
	Residue ^{ff}	0.41	0.41	0.41
Total			18.6	17.5

^a Total hydroperoxide titer of peroxide distillate C and benzene distillate B. However, glpc of triphenylphosphine-reduced distillates showed only 5.09 mmoles of 1-buten-3-ol and 2-buten-1-ol with 1-butene; 2.68 mmoles of alcohols found in 2-butene oxidation. ^b Assumed to be *trans* isomer. ^c Formation of equivalent water assumed. ^d Two incompletely resolved glpc peaks. ^e Formation of equivalent formaldehyde assumed but not detected (except as glycol formate in oxidations of butenes). ^f 262.5 mg, analyzing for C₄H_{7.40}O_{2.36} and containing 1.26 mmoles of RO₂H. ^g Does not include up to 0.9 mmole of crotonaldehyde which was not resolved from 1-buten-3-ol in this analysis. ^h 450 mg, analyzing for C₄H_{7.78}O_{2.18} and containing 1.60 mmoles of RO₂H. ⁱ 0.27 mmole of methyl alcohol found in reduced distillates. ^j 499.5 mg, analyzing for C₄H_{6.98}O_{1.60} and containing 0.754 mmole of RO₂H. ^k The ratio of tertiary to primary alcohol was 1.49 after Ph₃P reduction. ^l Alcohols corresponding to hydroperoxide. ^m Surmised from retention time. ⁿ 138.8 mg, contained 0.63 mmole of RO₂H, 92% of the theoretical for C₅H₉OOC₃H₁₀O₂H used for calculations. ^o mmoles of total alcohols were 1.70 tertiary + 1.44 secondary + 1.23 primary. ^p Up to 0.32 mmole of acetone came from ABN. For oxygen equivalent, the formation of acetaldehyde equivalent to AcMe from C₅H₁₀ is assumed. ^q 990 mg, analyzing for C₅H_{9.76}O_{2.18} and containing 3.80 mmoles of RO₂H. ^r The ratio of tertiary/primary alcohols was 18 after Ph₃P reduction. ^s 518 mg, analyzing for C₆H_{11.66}O_{2.26} and containing 1.80 mmoles of RO₂H. ^t The ratio of secondary/primary alcohol was 2.69 after Ph₃P reduction. ^u 628.4 mg, analyzing for C₆H_{11.81}O_{2.50} and containing 2.20 mmoles of RO₂H. ^v The ratio of secondary/primary alcohol was 1.33 after Ph₃P reduction. ^w 715 mg, analyzing for C₆H_{11.76}O_{2.37} and containing 2.56 mmoles of RO₂H. ^x CH₂O and CO are assumed to be the other corresponding carbon fragments. In another experiment, where permanent gases were sampled from the reaction bulb, 1.41 mmoles of CO, 0.20 mmole of CO₂, and 1.37 of mmoles H₂ per 12.8 mmoles O₂ consumed were found. ^y 235.5 mg, of material which partially crystallized on standing. Analysis of the oil fraction corresponded to C₆H_{10.35}O_{1.98}. ^z The ratio of primary/secondary alcohol was 2.91. ^{aa} For each *t*-BuOH, the formation of one acrolein is assumed. ^{bb} 0.59 mmole of H₂, 0.12 mmole of CO, and 0.05 mmole of CO₂ found by sampling gas above solution after reaction. ^{cc} For each acetone, the formation of one formaldehyde and one acrolein is assumed. ^{dd} 368.2 mg, analyzing for C₇H_{13.0}O_{1.47}N_{0.25} and containing 0.543 mmole of RO₂H. ^{ee} 380 mg, of material analyzing for C₆H_{9.66}O_{2.08} and containing 0.554 mmole of RO₂H. ^{ff} 47 mg, of material containing 0.188 mmole of RO₂H. ^{gg} Structure in accord with nmr spectrum.

effects on k_p' and k_p . This section now discusses that assumption.

Ingold has objected to this assumption, and has cited his data^{10b} which show that the termination

constant for 1-octene at 30° is 400 times that for tetramethylethylene. This difference seems improbably large to us since both 1-hexene (our analog) and tetramethylethylene yield allylic radicals which are not

Table II. Oxidations of Ethylene with 0.10 M Initiator in Benzene Solution at 70–130°

Reaction conditions				
Temp, °C	70	90	110	130
Time, hr	15.25	16.5	6.5	22
Vol. tube, ml	23.7	29.3	22.3 ^a	23.5
Benzene, g	2.68	2.76	2.72	2.71
Reactants, μmoles				
Initiator	305 ABN	310 ABC	309 ABC	308 <i>t</i> -Bu ₂ O ₂
Δ initiator ^b	264	265	309	244
C ₂ H ₄	30,050	29,900	30,150	30,850
O ₂ initial	1,711	2,048	2,823	2,682
O ₂ final	835	<i>c</i>	1330	465
Volatile products, μmoles (% ΔO ₂)				
CO	66 (6.8)	<i>c</i>	135 (9.1)	246 (11.2)
Formaldehyde	1.5 (0.15)	0.1	0 (0)	0 (0)
Formic acid	0 (0)	0	0 (0)	170 (15.4)
Ethylene oxide	3.2 (0.32)	17	39 (2.6)	332 (15.0)
Ethylene glycol	0 (0)	0	0 (0)	29 (2.7)
Trioxane	114 (11.7)	10	11 (0.7)	0 (0)
RO ₂ H	5 (0.5)	9	7 (0.5)	13 (0.6)
Residue				
Total, mg (% ΔO ₂)	42.3 ^d (40.8)	97.9	105.7	54.7
Analysis	C ₂ H _{3.25} O _{0.39} N _{0.38} ^d	C ₂ H _{2.98} O _{0.61} N _{0.26}		
Chain length, ΔO ₂ /1.2ΔIn	2.8		4.0	4.5 ^e

^a Ethylene pressure calculated from Raoult's law was 42 atm; calculated [C₂H₄] in liquid phase was 1.8 M. ^b Calculated from ref 8 and 9. ^c No gas analysis. ^d Corrected weight of C₂H₄ oxidation product, 19.8 mg; corrected analysis C₂H_{3.48}O_{1.9}. The correction assumes that the residue contains all the unreacted ABN, that 40% of the ABN decomposed appears as tetramethylsuccinonitrile (except for the 62 μmoles found by glpc in distillate), and that the remainder of the N in the residue is associated with initiator fragments as C₈H₁₂N₂O₂. ^e 100% efficiency assumed for *t*-Bu₂O₂.

Table III. Oxidations of Propylene in Benzene Solution at 60–110°

Reaction conditions				
Temp, °C	60	90	90	110
Time, hr	22	15	16	6
Vol. tube, ml	24.1	~100	22.4	24.9
Benzene, g	2.67	2.40	2.72	2.64
2.59				
Reactants, μmoles				
Initiator	305 ABN	283 ABC	309 ABC 942	304 ABC
Δ initiator ^b	254	213	263 acrolein	155
Propylene	30,000	30,700	30,400 added	30,400
O ₂ initial	1,269	1,196	2,054	10,628
O ₂ final	755	83	490	<i>c</i>
157				
Volatile products, μmoles (% ΔO ₂)				
CO	43 (5.7)	22 (1.9)	88 (5.6)	<i>c</i>
Acetaldehyde	15 (2.0)	35 (3.1)	36 (2.3)	44 (5.4)
Propylene oxide	26 (3.4)	182 (16.2)	224 (14.3)	43 (5.3)
Propylene glycol	13 (1.8)	5 (0.4)	23 (1.5)	0 (0)
ROOH	77 (10.1)	66 (5.9)	22 (1.5)	57 (7.1)
Acrolein	20 (2.6)	21 (1.9)	0 (0)	31 (3.8)
Acetone	8 (1.1)	15 (1.3)	14 (1.9)	0 (0)
X ₁ + X ₂ + cyclohexanone	14 (1.6)	68 (9.6)	31 (0.5)	7 (0.9)
91 (7.6)				
Residue				
Total, mg (% ΔO ₂)	60.4 (57.8)	53.6 (35.6)	180.8 (31.0)	104.0 (75.6)
Corrected, mg	21.4	30.8		
Analysis	C ₃ H _{5.1} O _{0.95} N _{0.72}	C ₃ H _{4.5} O _{1.06} N _{0.25}	C ₃ H _{4.9} O _{0.55} N _{0.21}	C ₃ H _{4.1} O _{0.49} N _{0.63}
Corrected analysis ^d	C ₃ H _{6.9} O _{2.6}	C ₃ H _{4.8} O _{1.45}		C ₃ H _{5.1} O _{0.71} N _{0.24}
Chain length, ΔO ₂ /1.2ΔIn	1.6	4.4	5.0	7.4

^a Propylene pressure calculated from Raoult's law was 22 atm; calculated [C₃H₆] in liquid phase was 3.3 M. ^b Calculated from ref 8 and 9. ^c No gas analysis. ^d See footnote *d*, Table II.

expected to react exclusively through either primary or tertiary peroxy radicals. However, even if we admit a factor as large as 400 between the termination constants of the "primary" allylperoxy radical from 1-hexene and the "tertiary" allylperoxy radical from tetramethylethylene, the net effect on our comparisons of $k_p'/(2k_t)^{1/2}$ is a factor of only about 4. This small effect results because the denominator involves the square root of k_t and because of a partly compensating factor in the numerator. We wish to compare values of k_p' for an average peroxy radical with several alkenes. If the two allylperoxy radicals are as different as reported in chain termination, then we should

allow also for the primary radical being five times as reactive as the tertiary radical in chain propagation,^{10b} and correct the numerator accordingly. Since nearly all of our relevant data involve allylperoxy radicals which are at least partly primary, we consider that the differences among their termination constants are not large and that they are partly compensated by corresponding changes in propagation constants, so that our conclusions are semiquantitatively useful.

For comparison, the $k_p'/(2k_t)^{1/2}$ values in Table V were further modified by correcting for symmetry in 2-butene and tetramethylethylene by dividing the addition rate constants by 2. This procedure implies

Table IV. Initial Rates of Oxidation (RO_2)₀ of Acyclic Alkenes and Alkynes

Hydrocarbon	Reaction temp, °C	[ABN] or [ABC]*	[RH] ₀	[RO ₂] ₀ , M hr ⁻¹	$(k_p + k_p') / (2k_t)^{1/2}$, (M ⁻¹ hr ⁻¹) ^{1/2}	Hydrocarbon densities ^a		Auto-catalysis ^b
						20°	Reaction temp, °C	
Propylene	110	0.06	3.3 ^c	0.030	0.135
Ethylene	110	0.08	1.8 ^c	0.056	0.23
1-Butene	70	0.0093	3.32 ^c	0.0088	0.066	0.595	0.536	0
<i>trans</i> -2-Butene	70	0.0094	3.06 ^c	0.0131	0.106	0.604	0.545	0
Isobutylene	80	0.0122*	3.42 ^c	0.0068	0.095	0.594	0.522	0
3-Methyl-1-butene	70	0.0090	8.23	0.033	0.100	0.648	0.577	+
Trimethylethylene	60	0.0094	8.87	0.025	0.142	0.662	0.622	+
Tetramethylethylene	50	0.0096	8.13	0.041	0.517	0.712	0.684	++
2-Methyl-1-pentene	70	0.0096	7.56	0.018	0.059	0.682	0.636	+
1-Hexene	90	0.0089*	7.22	0.020	0.076	0.673	0.608	+
<i>t</i> -Butylethylene	90	0.0090*	6.97	0.0062	0.050	0.653	0.587	+
Neopentylethylene ^d	90	0.0098*	6.28	0.0101	0.043	0.682	0.617	++
1-Hexyne	70	0.0095	8.11	0.019	0.18	0.716	0.665	+++ ^e
3-Hexyne	60	0.0094	8.34	0.151	0.90	0.723	0.685	++

^a Extrapolations of literature values or calculated from parameters of J. Griswold and J.-N. Chew, *Ind. Eng. Chem.*, **38**, 364 (1946). ^b ++, +, and 0 signify strong, weak, and no autocatalysis, respectively. ^c Benzene solutions; densities used for benzene were d_{20} 0.879; d_{70} 0.825; d_{80} 0.813; d_{110} 0.78. Undiluted hydrocarbons were used in other experiments. ^d Different run than that used for product studies. ^e Initial acceleration followed by retardation.

Table V. Addition and Abstraction Mechanisms in Autoxidation of Acyclic Alkanes

Hydrocarbon	Reaction temp, °C	Mechanism		O ₂ acctd for, %	Ratios of rate constants at 70°, (M ⁻¹ hr ⁻¹) ^{1/2}			
		Abstn, % ^a	Addn % ^b		$(k_p + k_p') / (2k_t)^{1/2}$	$k_p' / (2k_t)^{1/2}$ (addn)	$k_p / (2k_t)^{1/2}$ (abst)	$k_p / (2k_t)^{1/2}$ per H
Ethylene	110	0	100	~60	0.045	0.022 ^e	0.000	0.000
Propylene	110	~50	~50	~70	0.027	0.014	0.013	0.004
1-Butene	70	64 ^c (71) ^d	26	99	0.066	0.017	0.049	0.025
<i>trans</i> -2-Butene	70	33 ^c (47) ^d	62	99	0.106	0.033 ^e	0.040	0.007
Isobutylene	80	14 ^c	81	103	0.063	0.051	0.012	0.002
3-Methyl-1-butene	70	90 ^f	6	110	0.100	0.006	0.094	0.094
Trimethylethylene	60	39	52	103	0.213	0.111	0.102	{0.018 ^g 0.008 ^g }
Tetramethylethylene	50	54	42	97	1.16	0.25 ^e	0.67	0.056
2-Methyl-1-pentene	70	35 (56) ^d	45	99	0.059	0.027	0.032	0.016 ^h
1-Hexene	90	48 (73) ^d	33	95	0.034	0.011	0.023	0.012
<i>t</i> -Butylethylene	90	~2 ⁱ	~100	79	0.022	0.022	0.000	0.000
Neopentylethylene	90	23 (40) ^d	54	75	0.019	0.011	0.008	0.004

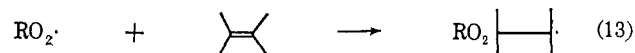
^a Per cent O₂ absorbed, titrated as hydroperoxide in the oxidation mixture before product separation. ^b Per cent of all alkene reacting and accounted for in Table I as products of addition mechanism, and half of the unidentified products. ^c In benzene solution after removal of olefin. ^d Plus alcohols and α,β -unsaturated $>C=O$. ^e $k_p' / (2k_t)^{1/2}$ divided by 2 for symmetrical olefins. ^f In oil remaining after removal of most of unreacted olefin. ^g 0.018 per Me hydrogen in =CHMe, 0.008 per Me hydrogen in =CMe, group. ^h In CH₂ group only. ⁱ From a different run than used for detailed product analysis.

that in all other cases, the alkylperoxy radical adds mostly to the least substituted side of the unsymmetrically substituted olefin.¹¹ By inspection of the corrected addition constants (in column 7 of Table V), it is seen that the values are readily grouped according to the substitution about the double bond as summarized in Table VI. If consideration is restricted to the methyl-substituted ethylenes and 1-butene (in lieu of propylene), one finds a good correlation of the addition rate constants with the calculated¹² excitation-energies, which are listed in Table VI. The excitation energy is the calculated difference between the ground-state singlet and the average energy of the first excited-state singlet and triplet. The correlation is shown in Figure 1.

The following discussion indicates that the transition state for addition lies intermediate between reactants and products.

(11) F. R. Mayo and C. Walling, *Chem. Rev.*, **46**, 264 (1950).(12) S. Sato and R. J. Cvetanović, *J. Am. Chem. Soc.*, **81**, 3223 (1959).

Also listed in Table VI are the calculated¹² free valences of the methyl-substituted ethylenes, and in the last column, estimated resonance (or hyperconjugation) energy changes for the process













The resonance energy for each hydrocarbon was calculated from data of Streitwieser¹³ and subtracted from the resonance energy of either the isopropyl ($RE = 0.297\beta_0'$) radical for the case of 1- and 2-butene or the *t*-butyl radical ($RE = 0.429\beta_0'$) for the case of isobutylene and tri- and tetramethylethylene. These relative energy changes assume a constant value for the energy of the carbon-oxygen bond formed in the process.

It is clear from inspection of the data and calculated values of Table VI that the rate constants for addition

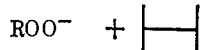
(13) A. Streitwieser, *ibid.*, **82**, 4123 (1960).

Table VI. Rate Constants for Addition of Peroxy Radicals and Molecular Orbital Parameters of the Alkenes

Type of substitution	Olefins	$k_p'/(2k_t)^{1/2}$	Excitation ^b energy, β_0	Free ^{a,b} valence	Olefin ^c resonance energy, $-\beta_0'$	ΔRE^c olefin radical, $-\beta_0'$
1		0.006	2.0113	0.759	0.442 ^d	0.145 ^d
		0.011				
		0.011				
		0.017				
		0.022				
1,1		0.051	1.9164	0.785	0.566	0.137
		0.027				
1,2		0.033 (0.066?)	1.9022	0.553	0.554	0.257
1,1,2		0.111	1.8100	0.577	0.669	0.240
1,1,2,2		0.25 (0.49?)	1.7242	0.378	0.776	0.347

^a At the less substituted carbon atom of unsymmetrical olefins. ^b Reference 12. ^c Reference 13, see text. ^d Propylene.

do not correlate well with either free valence or the calculated relative energetics of the over-all reaction. That rate constants correlate with excitation energy but not free valence is interesting in view of the results of Sato and Cvetanović¹² on the correlation of radical reactivities with olefins. They found a rough correlation for the additions of methyl, ethyl, and trichloromethyl radicals with the olefin's free valence, but for the additions of electrophilic reagents such as dibromocarbene, oxygen atoms (a diradical), and bromonium ion, excitation energy was a much better parameter for correlation. We take our results to indicate the electrophilic character of the peroxy radical and the ionic contribution of the transition state.



The lack of correlation with the estimated relative energy changes for the over-all process (13) indicates that the fully formed β -peroxyalkyl radical is a poor model for the transition state.

4. Rate Constants for Abstraction, $k_p/(2k_t)^{1/2}$. Rate constants for hydrogen abstraction as a function of alkene structure are considered in a similar manner in Table VII. Although reactivities per allylic hydrogen atom differ by a factor of nearly 50 (isopropylethylene vs. isobutylene), and although our results permit some refinements of Bolland's correlations,¹⁴ inductive and steric effects seem to preclude any simple correlations. The discussion below leads to the conclusion that a fully formed allyl radical + hydroperoxide is an inadequate model for the transition state of the abstraction reaction.

First, our over-all data in Table V are converted to a per allylic hydrogen atom basis in Table VII. With

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

only two alkenes need we consider more than one kind of reactive hydrogen atom. The products from 2-methyl-1-pentene show that the secondary allylic hydrogen is the principle allylic reaction site in this alkene. Since Table I shows that the ratio of second-

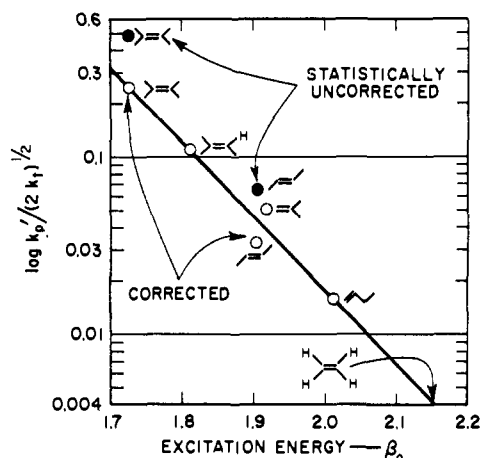




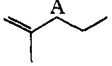


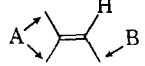



Figure 1. Rates of addition of alkylperoxy radicals to alkenes as a function of excitation energy.¹²

ary to tertiary allylic alcohol from 1,1,2-trimethyl-ene is 46:54, in the absence of data on the composition of the primary alcohol products we assume that 54% of the total hydrogen abstraction from this alkene comes from the 2-methyl group, 46% from the two 1-methyl groups.

We now consider the alkenes which we examined to be substituted propylenes, with 1, 2, and 3 substitution being defined in the heading of Table VII. Since the

Table VII. Relative Rates of Abstraction of Allylic Hydrogen Atoms from Substituted Propylenes

Olefin	Type of substitution	$k_p/(2k_t)^{1/2}$ per H atom
	3	0.025
	3	0.012
	3	0.004
	3 + 3	0.094
	2 + 3	0.016
	2	0.002
	1	0.007
	A: 1 + 2 B: 1 + 1	0.008 0.018
	1 + 1 + 2	0.056

data in this table refer to substitution only (in the absence of addition), we now reconsider Bolland's rules on this basis.

The results with the first three alkenes in Table VII illustrate our difficulties. They show that if R in $H_2C=CHCH_2R$ is methyl, propyl, or *t*-butyl, a sixfold difference in reactivity occurs. Steric effects seem to be involved, especially the number of 3 hydrogen atoms in the R group if the allyl hydrogen atom is taken as 1. The sensitivity of rate constants for hydrogen abstraction to conformation of cyclic alkenes was pointed out in our previous paper.²

Our data support Bolland's rule that substitution on the β position does not materially affect the $k_p/(2k_t)^{1/2}$ value. Thus 2-methyl-1-pentene is comparable to 1-hexene and attack on the "A" position of trimethylethylene comparable to 2-butene. The value found for propylene from the experiment, 0.004, is within experimental error of the 0.002 value of isobutylene. However, tetramethylethylene is exceptional. If we consider that trimethylethylene is a γ,α -disubstituted propylene, then β substitution (tetramethylethylene) increases reactivity by a factor of 3.

Bolland's rule that substitution by alkyl groups at either the α or γ position of the propylene will enhance the $k_p/(2k_t)^{1/2}$ values equally seems not to apply to our data. Thus, 1-butene is three times as reactive as 2-butene; 3-methyl-1-butene is more reactive than attack at "B" on trimethylethylene or, for that matter, attack on tetramethylethylene in spite of the presence of the additional alkyl group at β ; and 2-methyl-1-pentene is more reactive than the "A" hydrogens of trimethylethylene. These failures of Bolland's rule show that the transition state for the process



must lie considerably short of the fully formed allyl radical. This character of the transition state makes

difficult quantitative correlation to calculated energy differences of simple models. We note, however, that the discrepancies above are much smaller on a molecular than a per hydrogen basis.

5. Oxidations of Ethylene and Propylene. These alkenes reacted so slowly that yields and analyses are poor; further, they gave so much unidentified residues that assignments of mechanism are poorer than for other alkenes discussed here.

For ethylene we have the most information on the 70° experiment. Here 2.8 molecules of oxygen reacted per initiating radical; we would expect 0.5–1.0 molecule of O_2 to be absorbed by the initiator alone.¹⁵ The principal identified product was trioxane. From its composition, the residue could also contain a high proportion of formaldehyde units; 40% of the reacted oxygen is unaccounted for. The high ratio of formaldehyde (units) to ethylene oxide suggests that rather few peroxy radicals add to ethylene at 70° and that the principal chain carriers are hydroxy or alkoxy radicals.

At higher temperatures, the chains are somewhat longer. Ethylene oxide becomes the major identified product; formaldehyde disappears (except perhaps in the residue) and is replaced by CO. Apparently addition of alkylperoxy radicals becomes more important above 100°. As the conversions increase, formaldehyde is less able to survive. From its structure ethylene can react only by addition of radicals. The low peroxide titrations are presumably associated with secondary products.

Propylene also oxidizes slowly and material balances fail to account for up to 30% of the oxygen. Most of the oxygen accounted for is in the unidentified distillation residue (36–76%). The major volatile products are propylene oxide, glycol, and hydroperoxide. Carbon monoxide, acrolein, and acetaldehyde are minor products. As the reaction temperature increases from 60 to 110°, yields of epoxide + glycol increase and yields of hydroperoxide, acrolein, and residue decrease. At 90°, increased concentration of oxygen (obtained either by increasing the amount of oxygen or decreasing the size of the vessel) decreases the yield of epoxide and increases the yield of residue, as observed with several other alkenes. When acrolein was added initially, none was found in the products but the increased yield of residue approximated the amount of acrolein added. No volatile product was obtained from the residue in a Carbowax 20 M column at 150°. The infrared spectrum showed C–H bands at 3.5 μ , carbonyl at 5.75 μ , C=C at 6.75 μ , a weak HO band at 3 μ , and a C=N band at 4.5 μ . From elementary analyses, the residues are probably copolymers of acrolein and other oxidation products, with bound and unbound catalyst residues.

The increasing rate and yield of epoxide with increasing temperature reflect increasing participation of alkylperoxy radicals in the reaction. The decreasing yields of hydroperoxide and acrolein probably reflect their decreasing stabilities, the hydroperoxide decomposing into acrolein and the latter polymerizing and cooxidizing into residue. If, in the 110° experiments, we assign the carbon monoxide and acetaldehyde to the addition mechanism, then at least 37% of the oxygen accounted for (perhaps 50% of the propylene)

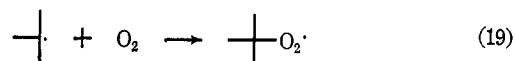
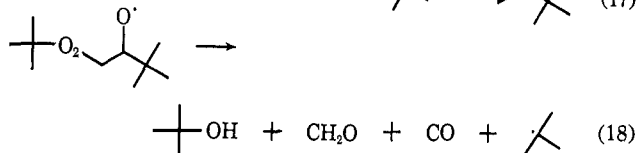
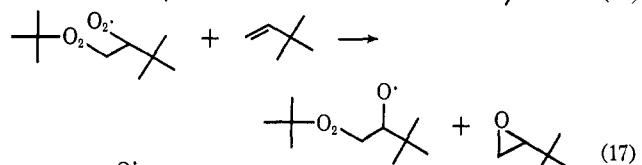
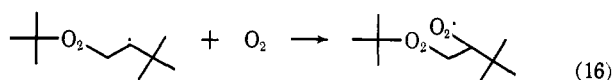
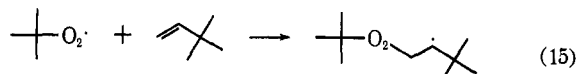
(15) M. Talat-Erben and N. Öno, *Can. J. Chem.*, **38**, 1154 (1960).

reacted by the addition mechanism. This result is consistent with at least 24% addition in the oxidation of 1-butene where the allylic hydrogen atom is more reactive than in propylene.

6. Oxidations of *t*-Butyl- and Neopentylethylenes. The oxidations of these alkenes are exceptional in giving products which are not predicted in eq 1-10.

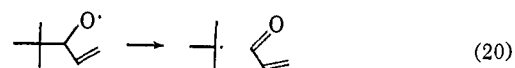
In spite of the absence of allylic hydrogen atoms, *t*-butylethylene was rather reactive in oxidation and more reactive toward addition of peroxy radicals than other more substituted ethylenes. The reaction was nearly self-sustaining; the final oxidation rate was nearly equal to the initial rate (~95%) in spite of 95% decomposition of the ABC. The aldehyde formed may be responsible.

To account for epoxide and *t*-butyl alcohol as main volatile products, the following chain sequence is proposed.



Step 18 proposes, in effect, that the β -peroxyalkoxy radical gives a *t*-butyl radical, formaldehyde, *t*-BuOH, and CO simultaneously. If the substantial concentration of a facile hydrogen donor (pivaldehyde) is never attained, the absence of acetone in the products seems to require the absence of free *t*-butoxy radicals. The yield of CO is below that of *t*-BuOH and the presence of hydrogen suggests additional complicating reactions.

Neopentylethylene provided the most complicated of all our oxidations. By no means could all the products be identified and the low oxygen balance suggests that some may have been missed; the presence of *t*-butyl alcohol, acetone, and acrolein suggests that the process (eq 20) plays an important part in the oxidation



mechanism. Both acrolein and *t*-butyl vinyl ketone might have contributed to the substantial residue found.

7. Oxidations of 1- and 3-Hexynes. 3-Hexyne oxidizes rapidly (~three times as fast as cyclohexene) and gave 67% yield of the propargylic hydroperoxide (structure based on alcohol found upon reduction). 1-Hexyne oxidizes ~five times as fast as 1-hexene. It gave only 17% yield of volatile hydroperoxide on the O₂ consumed but gave several unidentified volatile products. The reduction of the hydroperoxide with triphenylphosphine was inefficient (intense yellow color formed) and the amount of oxygen accounted for from the glpc of the reduced product was well below the amount absorbed by oxidation.

Effects of Experimental Variables in Oxidations of Alkenes¹

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Abstract: The yield of epoxide (*Y*) in olefin oxidations increases to a limiting value with decreasing oxygen pressure according to the relation, $Y = 1/(A + B[\text{O}_2])$. Such increases were observed in oxidations of cycloheptene, trimethylethylene, and cyclooctene. Rates of rearrangement of nine β -(alkylperoxy)alkyl radicals to epoxides are compared. The abstraction/addition ratio is nearly independent of temperature in oxidations of isobutylene and cycloheptene and of solvent changes in oxidations of cyclopentene, tetramethylethylene, and cyclooctene. Epoxide yields in cycloheptene oxidations are moderately higher at higher temperatures. Composite rate constants, $(k_p + k_p')/(2k_t)^{1/2}$, are increased 1.5-fold for each 10° temperature rise and up to fivefold by use of acetonitrile instead of benzene as solvent. For oxidations where little cleavage occurs, product yields do not depend much on conversion. Where aldehydes are produced, cooxidation of aldehyde and olefin may increase epoxide yields. Recent work on oxidation of alkenes is reviewed.

A previous^{2a} and an accompanying paper^{2b} discuss the products of oxidation of several alkenes in terms of the addition and hydrogen-abstraction mech-

anisms of oxidation. The present paper evaluates the importance of oxygen pressure, temperature, solvent, and conversion on the products of oxidation of some of these alkenes. Control of temperature and

(1) Research sponsored by AFOSR (SRC)-OAR, U. S. A. F. Contract No. AF49 (638)-1102.

(2) (a) D. E. Van Sickle, F. R. Mayo, and R. M. Arluck, *J. Am. Chem.*

Soc., **87**, 4824 (1965); (b) D. E. Van Sickle, F. R. Mayo, R. M. Arluck, and M. G. Syz, *ibid.*, **89**, 967 (1967).