[CONTRIBUTION FROM THE GENERAL ELECTRIC RESEARCH LABORATORY AND STANFORD RESEARCH INSTITUTE]

The Oxidation of Unsaturated Compounds. VIII. The Oxidation of Aliphatic Unsaturated Compounds[1,*]

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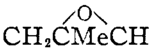
This work confirms the earlier report that the autoxidation of 2,4,4-trimethyl-1-pentene near 100° gives epoxide and ketone as major products, and hydroperoxide only as a minor product. This result is independent of oxygen pressure over a range of oxygen pressures from 1–120 mm. Some of the literature on oxidation of aliphatic compounds is reviewed, with the conclusion that hydrocarbons of the structure $RR'C{=}CH_2$ give the most epoxide and least hydroperoxide on autoxidation. Allylic hydroperoxides are major oxidation products of most aliphatic monoölefins of other structures, but epoxides and cleavage products also appear. An explanation for these results is presented.

13. Introduction

Most aliphatic unsaturated hydrocarbons are considered to give 60–100% of allylic hydroperoxides as major products of low-temperature liquid-phase oxidations.[11,12,69] Papers I, V and VI have shown that the oxidations of styrene and α-methylstyrene give polyperoxides and also substantial proportions of epoxides, aldehydes and ketones when carried out at low pressures of oxygen. The report of Gasson and co-workers,[70] that the oxidation of α-diisobutylene, 2,4,4-trimethyl-1-pentene, with air or oxygen at 140° gave epoxide ( $t\text{-BuCH}_2\overset{O}{\text{CMeCH}_2}$) and ketone ($t$-BuCH$_2$COMe) as major primary products, and hydroperoxide only as a minor product, raised the questions: (1) Is the formation of epoxide from diisobutylene a low-pressure phenomenon? (2) What are the implications of this reaction for oxidations of aliphatic unsaturated compounds in general?

14. Experimental

14.1. General Procedure.—One hundred ml. (70.4 g.) of α-diisobutylene (separated from the β-isomer by Dr. N. C. Cook), 0.80 g. of redistilled t-butyl perbenzoate and 0.5 or 1.0 g. of magnesium oxide (to neutralize acidity) were stirred vigorously and heated with a glass mantle to gentle reflux for 4 (expts. 5, 6, 9), 6 (expt. 8) or 8 (expt. 10) hours. Oxygen or air was passed through the system, with flowmeters to measure the input and output of gas. The vapors from the reaction mixture were passed through an ice-cooled reflux condenser and then through a trap at −78°, the latter to remove diisobutylene before the gases passed through the exhaust flowmeter. The pressure of air or oxygen above the reaction mixture was measured by the boiling point depression due to gas flow. Experiment 11 was carried out in a 60° thermostat for 24 hours.

Equilibrium is assumed between the vapor and liquid, in view of the vigorous stirring and low rate of oxygen consumption. The epoxide and neopentyl methyl ketone were determined by infrared absorption of the whole reaction mixture. t-Butyl perbenzoate was determined in the concentrate of the reaction mixture. Hydroperoxides were determined by titration of the same concentrate, correcting for the t-butyl perbenzoate. The remaining high-boiling materials were determined by difference. The latter determination is obviously subject to considerable error, but these products usually were found in unimportant proportions.

14.2. Measurement of Gas Pressure.—The pressure measurements depend on a 75 mm. immersion thermometer calibrated in tenths of a degree. The bulb and about 75 mm. of the stem were constantly immersed in, or sprayed with, stirred liquid. In addition, about 30° of the stem was in refluxing vapors, so that readings about 0.4° high should be expected. Since we are concerned with temperature differences, and since the length of stem in refluxing vapor was constant, corrections for immersion and barometric pressure are neglected.

The observed initial boiling points (*i.e.*, reflux temperatures, with good stirring, and no passage of gas) of α-diisobutylene ranged from 101.2° at 741 mm. to 101.6° at 751 mm. Similar measurements at slightly reduced pressures showed that the boiling point decreased one degree for every 20 mm. change in pressure over the range 670–750 mm., one degree for every 18 mm. over the range, 580–670 mm., and one degree for every 16 mm. just below 580 mm. Since boiling point depressions were reproducible to ±0.1°, gas pressures up to 50 mm. were known to ±2 mm.

The initial boiling points were depressed by the passage of gas, and the depression measures the contribution of the gas to the total pressure above the reaction mixture. Since the boiling point at zero gas flow rose from 0.2 to 0.7° during an oxidation, the boiling point depression due to flow of gas was measured at the beginning and end of an oxidation, and sometimes once or twice during an oxidation (by shutting off gas flow for about 5 minutes, measuring the rise in reflux temperature, and correcting the reaction time). The average depression was used to measure the gas pressure over the solution and may have varied, or be in error, by ±10% in a single experiment.

Flow rates were measured by capillary flowmeters and dibutyl phthalate manometers, calibrated for both oxygen and nitrogen by the use of gas burets. The flow rate for nitrogen for a given pressure difference was 15% higher than for oxygen (as found by others). The flow rate was a linear function of the pressure difference and was assumed to be a linear function of the proportions of oxygen and nitrogen. The flowmeters could be read to ±0.5 ml./minute.

Whether oxygen or air was introduced, the gas pressure was taken directly from the boiling point depression. When air was introduced, the proportion of oxygen in the exit gas (considered to be representative of that over the reaction mixture) was calculated from the amount of gas absorbed.

14.3. Analyses.—The reaction vessel (originally containing 70.4 g. of diisobutylene, 0.80 g. of t-butyl perbenzoate and 0.5 or 1.0 g. of magnesia) lost weight during reaction; 0.5–2.2 g. of condensate was collected in the trap at −78°, and 0.5–5.0 g. more was unaccounted for. The losses were lowest in expts. 9 and 11, with the lowest gas flows. Losses were highest in experiments with a high flow rate (expt. 5), or a long reaction time (expt. 10). The losses are assumed to be essentially diisobutylene, the most volatile of the products considered.

The final reaction mixture was filtered or decanted from magnesia and a few grams was reserved for determination of ketone and epoxide by infrared absorption. The remaining weighed fraction was concentrated up to a liquid temperature of about 50° at 30 mm. pressure. The weighed concentrate was analyzed by infrared for other products.

14.4. Determination of Epoxide and Ketone.—Ketone and epoxide for infrared standards were obtained from combined oxidation products by fractional distillation at 100 mm. pressure through a 20-cm. column with a platinum spiral packing. Their boiling points agreed satisfactorily with those of Gasson, *et al.*[70] Analyses for epoxide and ke-

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* For numbering of footnotes, equations, etc., *cf.* note 2 of paper V

(69) W. A. Waters, "Organic Chemistry," edited by H. Gilman, John Wiley and Sons, Inc., New York, N. Y., Vol. IV, 1953, p. 1138.

(70) E. J. Gasson, A. F. Millidge, G. R. Primavesi, W. Webster and D. P. Young, *J. Chem. Soc.*, 2161 (1954); British Patent 682,067 (1952); U. S. Patent 2,650,927 (1953). British Patent 708,913 (1954) relates to improving yields of epoxides by removing the acids formed in oxidation.

tone were carried out on the final reaction mixtures, without correction for volume change during reaction. Because of the small conversions and low absorptions by the products, stated concentrations of epoxide and ketone may be in error by as much as 10%, but comparisons of experiments should be more reliable.

14.5. Determination of Other Products.—The residues from concentration of the reaction mixtures contained some diisobutylene and part of the ketone and epoxide formed. They are assumed to contain all of the peroxides and all of the higher-boiling oxidation products formed. These residues were analyzed for diisobutylene, neopentyl methyl ketone, epoxide and *t*-butyl perbenzoate by infrared absorption, using the appropriate standards. Errors in these determinations may range up to 20%. The remaining material is assumed to be hydroperoxide, $C_8H_{15}O_2H$, and other higher-boiling products.

TABLE XIV

OXIDATION OF α-DIISOBUTYLENE AT VARIOUS OXYGEN PRESSURES

Expt.	Average[a] temp., °C.	Oxygen pressure,[b] mm.	Average rates of formation, mole/l./hr. Ketone[c]	Oxide[d]	$C_8H_{15}O_2H$[e]	Other	Total
			0.04 *M* *t*-Butyl perbenzoate added initially				
8	95.5	120[g]	0.019	0.021	0.006	0.0003	0.046
6	99.5	46[g]	.026	.034	< .008	[f]	.068
5	99.4	9[i]	.017	.030	< .009	[f]	.056
9	101.4	<0.5[j]	.013	.016	.008	None	.037
			No initiator added				
10	99.6	43[g]	0.0066	0.0075	0.0027	0.002	0.019
			0.01 *M* ABN added initially				
11	60.0	~500[h]	0.0010	0.0011	0.0006	0.0010	0.0037

[a] Temperature of stirred reaction mixture. [b] Pressures were measured by boiling point depression. [c] Neopentyl methyl ketone. [d] 2,4,4-Trimethyl-1,2-epoxypentane. [e] Easily reducible peroxide, assumed to be the allylic hydroperoxide, $C_8H_{15}O_2H$. [f] Other compounds, by difference, in distillation residue, converted to moles/l. as if they were all the monoformate of diisobutylene glycol. In expts. 5 and 6, peroxide was not determined, and the rates given for peroxide formation corresponded to combined rates of formation of hydroperoxides plus "other compounds." [g,h] Oxygen supply, 50[g] or 4.15[h] ml./min. [i,j] Air supply, 50[i] or 10[j] ml./min.

Peroxides in the residue were determined with sodium iodide and acetic acid in refluxing isopropyl alcohol, according to the procedure of Wagner, Smith and Peters,[71] using a 5-min. reflux time. After all the peroxide determinations had been run and the samples were exhausted, it was found that only 33% of the *t*-butyl perbenzoate was reduced in the 5-minute reaction time (in a reaction which continued according to a first-order rate law). Accordingly, the hydroperoxide reported is the difference between the total peroxide found by titration and 33% of the *t*-butyl perbenzoate found by infrared. Some unknown material containing hydroxyl and carbonyl groups was unaccounted for in some experiments. For a rough estimate of the importance of this material as a product, it is assumed to be the monoformate of the glycol of diisobutylene, not inconsistent with the more careful investigation by Gasson, *et al.*[70] Since several errors accumulate in the estimation of the amount of this material, it is not certain that the differences in the quantities reported are significant. However, this material was a minor product in all reactions with initiator at 100°. After the fraction of each product in the distillation residues had been estimated, each fraction was converted to grams in the portion of the reaction mixture taken for concentration. In Table XIV, these weights have then been corrected to moles/liter in the final reaction mixture, taking the density of each reaction mixture as 0.704, the observed density of diisobutylene at room temperature. The observed conversions have been divided by the reaction times to give average rates in Table XIV, with no allowance for autocatalysis, if any.

14.6. Estimation of Kinetic Chain Lengths.—This section gives the details for estimating kinetic chain lengths in the oxidation of diisobutylene at 60 and 102°. The rate of decomposition of *t*-butyl perbenzoate was measured in refluxing diisobutylene (102–104°), using phosphoric acid and sodium iodide in acetic acid[72] to follow the peroxide concentration.[73] Over the first third of the decomposition of a solution originally 0.035 *M* in *t*-butyl perbenzoate, the apparent first order rate constant was about 0.094/hr. This value is in the range indicated by the work of Blomquist and Ferris.[72] In the experiments in Table XIV, with an initial peroxide concentration of about 0.04 *M* and a temperature of 99°, peroxide should decompose at the rate of 0.003 mole/l./hr. The rate of oxidation is about 0.06 mole/l./hr. Since initiation is less than 100% efficient, at least 20 hydrocarbon molecules are oxidized per pair of chain-initiating radicals from the perbenzoate. However, expt. 10, with no catalyst added, suggests that as much as half of the initiation may come from autocatalysis after a few hours of reaction.

The rate of decomposition of ABN at 60° in benzene or styrene is 0.042/hour.[9,74] In 0.01 *M* solution, the initiator should decompose at the rate of 0.00042 mole/l./hr. The observed rate of oxidation of diisobutylene (Table XIV) is 0.0037 mole/l./hr. Thus, at least nine molecules of hydrocarbon are oxidized per radical pair liberated by the initiator, but autocatalysis by the hydroperoxide formed may make this kinetic chain length too high.

15. Results and Discussion

15.1. The Effect of Oxygen Pressure on the Oxidation of α-Diisobutylene.

—α-Diisobutylene has been oxidized at 95–102°, at oxygen pressures from 120 mm. to less than 1 mm., in the presence of 0.041 *M* *t*-butyl perbenzoate as initiator. Data are summarized in Table XIV. When allowance is made for temperature changes, the total rate of oxidation of diisobutylene is nearly independent of oxygen pressure above 10 mm. pressure, but decreases below this pressure. This type of behavior is typical of hydrocarbon oxidations.[11,12] Over the whole pressure range, the proportion of oxidation products formed is constant within experimental error: 43–54% of epoxide, 30–41% of ketone (by cleavage of the double bond), and only 13–20% of hydroperoxide and other products. At 60°, with 0.01 *M* ABN as initiator, the oxidation is much slower. Oxide and ketone are still major products, and hydroperoxide is still a minor product, but more "other products" are found than at

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(71) C. D. Wagner, R. H. Smith and E. D. Peters, *Anal. Chem.*, **19**, 979 (1947).

(72) A. T. Blomquist and A. F. Ferris, THIS JOURNAL, **73**, 3408, 3412 (1951).

(73) Unpublished work by Mr. A. T. Tweedie.

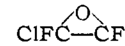
(74) C. E. H. Bawn and S. F. Mellish, *Trans. Faraday Soc.*, **47**, 1216 (1951).

100°. This experiment at 60° shows that the difference in oxidation behavior between diisobutylene and previous model alkenes, studied mostly below 100°, is not a temperature effect. Since epoxide and ketone are primary products at 140°,[70] they are also primary products at 60 and 100°.

The results reported here support the conclusions of Gasson, *et al.*,[70] that oxide and ketone are major products and that hydroperoxide is a minor product. The oxidation of diisobutylene is still a free radical chain reaction, since it is definitely slower, but probably autocatalytic, in the absence of added initiator. Chain lengths are short. Comparison of rates of decomposition of the initiators with the rates of oxidation of diisobutylene indicate that about ten hydrocarbon molecules are oxidized per initiator molecule decomposed at 60°, about 30 at 100°. The indicated chain lengths may be still lower when allowance is made for autocatalysis. These statements are documented in section 14.6.

15.2. The Oxidation of Other Aliphatic Unsaturated Compounds.—The generally accepted conclusion that the liquid-phase oxidation of aliphatic monoölefins gives mostly hydroperoxides is based mostly on work with cyclohexene and rubber models. Farmer and Sundralingham[75] obtained a little cyclohexene oxide along with the hydroperoxide, but concluded, on inadequate evidence, that the epoxide arose from reaction of cyclohexenyl hydroperoxide with cyclohexene. However, this route to epoxides has not yet been generally excluded, except with α-diisobutylene and polychloroethylenes.

A brief check of the oxidation literature has shown that formation of epoxides and cleavage products is not an uncommon phenomenon in aliphatic oxidations. Such products have been mentioned for hexenes,[76] α-pinene,[77] 10,11-undecylenic acid,[78] oleic[79,80] and elaidic acids,[79] and mesityl oxide.[81] Glycols, presumably arising from epoxides by hydrolysis, have been obtained from cyclohexene,[76] undecylenic acid,[78] oleic acid,[80] and isobutylene.[82] In the last instance, 59% yield of isobutylene glycol was reported at 135° in a water-benzene mixture. With mesityl oxide,[81] the epoxide was the product formed in largest proportion. Epoxides have been reported as primary products in the autoxidation of trichloroethylene[83] and tetrachloroethylene.[84,85] These epoxides are easily rearranged to acid chlorides. The formation of oxalic acid from chlorotrifluoroethylene, oxygen and water, observed by Myers,[86] may now be considered to proceed through the epoxide


$$\mathrm{ClFC\overset{O}{—}CF_2}$$

Some effects of structure on the products of oxidation of aliphatic monoölefins have been reported recently by two independent groups. Hawkins and Quin[87] oxidized hydrocarbons at about 100° in the presence of magnesia (to remove acids), and about 0.01% cobalt naphthenate. Sometimes *t*-butyl hydroperoxide was added. They reported various proportions of aldehyde and ketone cleavage products, the corresponding acids, epoxides, glycols, 1,2,3-triols, allylic alcohols, allylic carbonyl compounds, esters, hydroperoxides and degradation products. The results are complicated by the effect of the cobalt on the hydroperoxides, leading to both alcohols and cleavage products. The data indicate that most hydrocarbons with one to four alkyl groups on the doubly-bound carbon atoms give allylic hydroperoxides as major primary products, but that epoxides and cleavage products always appear. Yields of hydroperoxides were particularly high with methylcyclohexenes. Epoxide was the major product with 2-methyl-1-nonene. Since epoxide was also the major product from α-diisobutylene,[70] the structure $\mathrm{RCMe{=}CH_2}$, seems to be especially favorable for epoxidation. The olefin, *t*-BuCH=CH-*t*-Bu, without allylic hydrogen atoms, could not be oxidized under the standard conditions.

Hargrave and Morris[88] measured oxygen absorption by twenty olefins in the absence of catalysts at 35–75°. The fraction of oxygen appearing as hydroperoxide was determined by titration. The remainder of the oxygen was assumed to be present as dialkyl or polymeric peroxides which were not titrated. The highest yields of hydroperoxides were obtained from olefins with internal double bonds. By far the lowest yield of hydroperoxide was reported for 2-methyl-1-nonene. Scission products accounted for only a small proportion of the reacting oxygen, and the work of others suggests that epoxide was a major product.

15.3. Mechanisms of Oxidation.—Twigg[89] has proposed a reasonable mechanism for epoxide formation: peroxide radicals add to ethylene bonds (reaction 4) instead of removing allylic hydrogen atoms, (reaction 16). The resulting radical then splits off an epoxide unit (reaction 8), and the alkoxy radical continues the oxidation chain (becoming an alcohol or part of an ether) or possibly splits off another epoxide unit. Support and amplification of this proposal are now offered. Relative reactivities of polysubstituted ethylenes in copolymerization[16] show that 1,1-disubstituted ethylenes, $\mathrm{R_2C{=}CH_2}$, are in general much more re-

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(75) E. H. Farmer and A. Sundralingham, *J. Chem. Soc.*, 121 (1942).

(76) H. G. Schneider and J. V. Sommer, U. S. Patent 2,052,195 (1936).

(77) R. N. Moore, C. Golumbic and G. S. Fisher, This Journal, **78**, 1173 (1956).

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(81) E. G. E. Hawkins, *J. Chem. Soc.*, 3288 (1955).

(82) C. E. Schweitzer, U. S. Patent 2,644,837 (1953).

(83) M. Mugdan and J. Wimmer, U. S. Patent 1,976,265 (1935); F. W. Kirkbride, U. S. Patent 2,292,129 (1942); L. L. McKinney, E. H. Uhing, J. L. White and J. C. Picken, Jr., *J. Agric. Food Chem.*, **3**, 413 (1955).

(84) C. Schott and H.-J. Schumacher, *Z. physik. Chem.*, **B49**, 107 (1941); F. W. Kirkbride, U. S. Patent 2,321,823 (1943).

(85) D. M. Frankel, C. E. Johnson and H. M. Pitt, *J. Org. Chem.*, **22**, 1119 (1957).

(86) R. L. Myers, *Ind. Eng. Chem.*, **45**, 1783 (1953).

(87) E. G. E. Hawkins and D. C. Quin, *J. Appl. Chem. (London)*, **6**, 1 (1956).

(88) K. R. Hargrave and A. L. Morris, *Trans. Faraday Soc.*, **52**, 89 (1956).

(89) G. H. Twigg, *Chem. Eng. Sci. Suppl.*, **3**, 5 (1954). References 70, 87 and 89 are all from the same laboratory, The Distillers Company Ltd.

active in additions of radicals than are the 1-, 1,2-, 1,1,2- or 1,1,2,2-substituted ethylenes. Therefore the most addition, and the least transfer of allyl hydrogen atoms, should be expected in the reaction of peroxide radicals with $RCMe{=}CH_2$. Here, the most epoxides[87] and least peroxides[88] have been observed in autoxidation. With any other arrangement of alkyl radicals, hydrogen transfer predominates over addition. When phenyl, vinyl, carbonyl or nitrile groups are attached to an unsaturated carbon atom, then addition predominates. Oxidations of such compounds are reviewed in section 17. With styrene and α-methylstyrene, the monomer radical is resonance-stabilized, and its life must be prolonged (at 50°, but not at 170°) by reducing the oxygen pressure, to observe much formation of epoxide. However, when the β-peroxyalkyl radicals are not resonance-stabilized, as in the case of α-diisobutylene, the rearrangement to epoxide occurs so fast that it is unaffected by oxygen at 100° at pressures below 120 mm. Perhaps superatmospheric pressures of oxygen will retard formation of epoxide and thus permit further growth of the radical and more cleavage by depolymerization. Depending on its length and structure, the alkoxy radical resulting from reaction 8, in addition to the hydrogen transfer and possible epoxide formation reaction mentioned by Twigg, may also split out formaldehyde or some other carbonyl compound. Thus, cleavage products should accompany epoxidation.

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The Oxidation of Unsaturated Compounds. IX. The Effects of Structure on the Rates and Products of Oxidation of Unsaturated Compounds[1,*]

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The relative rates of reaction of some unsaturated compounds with one atmosphere of oxygen have been investigated, using one monomer at a time, and using two monomers at a time (to yield a terpolymer with oxygen). The close correspondence between the two sets of data indicates that the reactivity of the double bond toward a peroxide radical is the principal factor governing the over-all rate of reaction. The organic part of the peroxide radical (M in $MO_2\cdot$) has a small but significant effect on the propagation reactions of the peroxide radical. The products of oxidation of unsaturated compounds are considered, using the data in this report and in the literature. The critical factor is the predominance of addition of $MO_2\cdot$ to M, or of abstraction of an allylic hydrogen atom from the monomer by the peroxide radical. Addition is favored when the double bond is conjugated with an aromatic, carbonyl, nitrile or another vinyl group, or when the unsaturated compound contains no allylic hydrogen atoms (as in vinyl acetate). The products are then polymeric peroxides, cleavage products and epoxides. Two mechanisms for cleavage have been distinguished, only one of which is sensitive to oxygen pressure. The rates of thermal oxidation of indene, α-methylstyrene and styrene are compared with respect to both the initial and the autocatalytic oxidations. Indene is outstanding in both reactions. The effect of oxygen on rates of polymerization of various monomers is considered. Reactions of polyperoxides are reviewed briefly.

16. Rates of Oxidation

16.1. Rates of ABN-initiated Oxidations.—This section will show that the relative reactivity of the double bond toward radicals, as measured by copolymerization, is the principal factor determining the relative rate of oxidation of an unsaturated compound. Table XV compares the initial rates of oxidation of thirteen unsaturated compounds, mostly with conjugated phenyl or unsaturated groups, in the presence of 0.01 *M* ABN and one atmosphere of oxygen[90] at 50°. The first column of figures gives the rate of oxygen absorption in moles/l. of solution/hr. The next column corrects these figures to 1 *M* monomer in each solution and determines the order of listing of the compounds in Table XV. These *k* values are composites of the initiation efficiencies, the termination constants and the rates of chain propagation. The rate-determining step in the propagation is reaction 4, the addition of a peroxide radical ($MO_2\cdot$) to the double bond. Table XV suggests that this reaction 4 is the most important factor governing the *k* values. The hydrocarbons where phenyl groups are conjugated with the double bonds are usually much more reactive than those without such conjugation. The order of the *k* values, the expected reactivities of the double bonds toward $MO_2\cdot$ radicals, and the reactivities of the same monomers toward other electron-accepting radicals (*e.g.*, those from acrylonitrile or maleic anhydride), as determined from copolymerization data,[16] are all qualitatively similar.

The effects of β-substituents in styrene are now considered. While a 2-substituent in a 1-substituted ethylene usually decreases the ease of attack of a double bond by an approaching radical, a smaller or an opposite effect may be observed if a polar effect is enhanced by the 2-substituent.[16] Table XV shows that a β-methyl group decreases only slightly the reactivity of the styrene double bond toward a peroxide radical, while a β-bromine atom is an obstacle to reaction with peroxide radicals (and also with styrene radicals).[91] These results are consistent with the view that the peroxide radical is an electron acceptor and prefers to react with electron-donor double bonds.

Dyer and co-workers[92] have recently indicated the following order of rates of oxidation in aqueous persulfate solution at 50°: methacrylonitrile > methyl isopropenyl ketone > methyl vinyl ketone

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[*] For numbering of footnotes, equations, etc., *cf.* note 2 of paper V.

[90] The total pressure was about 750 mm. Correction for monomer vapor pressure has been neglected in this table.

[91] M. H. Jones, *Can. J. Chem.*, **34**, 108 (1956).

[92] E. Dyer, O. A. Pickett, Jr., S. F. Strause and H. E. Worrell, Jr., THIS JOURNAL, **78**, 3384 (1956).