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.

MENLO PARK, CALIFORNIA

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

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

BY FRANK R. MAYO,[3] A. A. MILLER AND GLEN A. RUSSELL

RECEIVED SEPTEMBER 5, 1957

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

---

[*] 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).

TABLE XV

INITIAL RATES OF ABSORPTION OF OXYGEN (R_O) BY UNSATURATED COMPOUNDS AT 50°

(0.01 M ABN, one atm. oxygen, no solvent)

Unsaturated compound	Rates in moles/l./hr. R_O[a]	$100k$[b]	R_p[c]	R_C[d]	R_C/R_O
α-Methylstyrene	0.113[e]	1.58	0.071	0.040	0.36
Indene[6]	.081	.97	.081	~0	~0
Styrene	.060	.71	.057	0.003	0.05
β-Methylstyrene	.027	.37	.010[f]	0.017[f]	
1,1-Diphenylethylene	.018	.31	[j]	[j]	~2
Acrylonitrile	.018	.10	[j]	[j]	
Allylbenzene	.0059	.079	~ .0059[g]	~0	~0
Methyl methacrylate[h]	.0062	.069	0.0049	0.0013	0.21
Butyl methacrylate	.0039	.062			
Vinyl acetate	.0662	.057	[g]		
Acenaphthylene	.00066[i]	.033	[i]		
Butyl acrylate	.0013	.019			
β-Bromostyrene	<.0001	<.001			

[a] Rate of oxygen absorption. [b] k = rate of oxygen absorption/molar concentration of pure monomer. [c] Rate of formation of peroxide. [d] Rate of formation of either carbonyl cleavage product. [e] Includes 0.002 mole/l./hr. of oxygen in α-methylstyrene oxide. [f] Assuming that no aldehydes found in the final analysis arise from decomposition of polyperoxide. [g] Cinnamyl hydroperoxide.[12] [h] 8-hour rates in expt. 1, Table XII. [i] Measured rate was 0.0021 for 2 M solution in chlorobenzene containing 0.10 M ABN. Stated rates have been corrected to 0.01 M initiator. No peroxide was precipitated from the product by methanol. [j] Product cited in literature review.

> acrylonitrile > acrylamide > methyl acrylate. They have noted the polar effects of the substituents and have concluded that the monomers which are the poorest electron donors oxidize at the lowest rates.

16.2. Rates of Thermal Oxidations.—Initial rates of thermal oxidation at 50° (no ABN) can be compared for three monomers. Equations 48, 54 and 55 give the rates of reaction with oxygen at 1 atmosphere in moles per liter of undiluted monomer per hour.

Indene $$d[O_2\text{ absbd.}]/dt = (0.00090 + 0.0354\ [O_2\text{ absbd.}])^{1/2} \quad (54)$$

Styrene $$d[O_2\text{ absbd.}]/dt = (0.000014)^{1/2} \quad (55)$$

α-Methylstyrene $$d[O_2\text{ absbd.}]/dt = (0.0000018 + 0.00063\ [O_2\text{ absbd.}])^{1/2} \quad (48)$$

The indene equation was calculated from original data,[6] the styrene equation comes from paper I,[4] and equation 48 is repeated from section 8.6. The three monomers are arranged in the order of decreasing initial rates of oxidation. The first terms on the right sides of the equations are proportional to the rates of thermal initiation and to the squares of the initial rates of oxidation. The second terms are proportional to the rates of initiation by the peroxide formed. The autocatalysis with indene and α-methylstyrene may be associated with the formation of a little allylic hydroperoxide, not possible with styrene, and perhaps also with traces of metals (paper VI). The relatively high rates of both spontaneous and autocatalytic oxidation of indene are probably associated with the higher activity of ring hydrogen atoms[93] and the high proportion of hydroperoxide. The initial rate of the thermal oxidation of methyl methacrylate was well below 10% of the styrene rate.

16.3. The Effect of Oxygen on Rates of Polymerization.—This section will compare the rates of reaction, by a free radical mechanism, of some polymerizable and non-polymerizable monomers in the presence and absence of oxygen. There are three factors to be considered. First, the products of reaction depend on the presence of oxygen. Second, free radicals are excellent scavengers for oxygen, and the effect of oxygen sometimes depends on its concentration. Third, both polymerization and oxidation involve similar radicals, and homopolymer and copolymer cannot be formed independently if oxygen is present.[6] Autocatalysis by oxidation products is considered in section 16.2.

Table XVI shows the rates of reaction of several unsaturated compounds in the presence of 0.01 M ABN at 50°. In the absence of oxygen, the products, if any reaction occurs, are simple polymers. In the presence of a steady supply of oxygen at a total pressure of one atmosphere, the polymeric products are essentially 1:1 copolymers with oxygen. In the cases of monomers which exhibit little or no polymerization in the absence of oxygen, reaction becomes possible, or much faster, in the presence of oxygen. Here, clearly, the ratio $k_p/k_{tm}^{1/2}$ is much *less* favorable to reaction than the ratio $k_{pm}/k_{to}^{1/2}$. The monomers which polymerize fastest, vinyl acetate, acrylonitrile and methyl methacrylate, react much slower in the presence of oxygen. Here, the ratio $k_p/k_{tm}^{1/2}$ is much *more* favorable to reaction than the ratio $k_{pm}/k_{to}^{1/2}$. For the conditions shown in Table XVI, the rate of reaction of styrene is nearly the same in the presence and absence of oxygen. Inspection of Table XVI suggests that, to a first approximation, the polymerizations of monomers which polymerize the fastest in the absence of oxygen are retarded the most by oxygen. These are the monomers with the most reactive radicals and least reactive

TABLE XVI

EFFECT OF OXYGEN ON RATES OF REACTION OF MONOMERS (R_M) AT 50° IN THE PRESENCE OF 0.01 M ABN

Monomer	Init. rate of reaction in moles/l./hr. O_2 absent	O_2 at 1 atm.	Rate with O_2 / (Rate without O_2)
Vinyl acetate	2.2[a]	0.0062	0.0028
Acrylonitrile	0.7 to 1.0[b]	.018	.02
Methyl methacrylate	.40	.0065	.016
Styrene	.095	.060	.63
Indene	.0031[c]	.081	26
β-Methylstyrene	0	.027	Very large
α-Methylstyrene	0	.115	Very large

[a] Calculated from $k_p^2/2k_t$ of M. S. Matheson, E. E. Auer, E. B. Bevilacqua and E. J. Hart, THIS JOURNAL, 71, 497 (1949), and the assumption that the rate of initiation is twice the rate of decomposition of ABN. [b] Extrapolated to 15 M nitrile from rates for homogeneous polymerization of 1.66 M monomer in N-dimethylformamide and in ethylene carbonate, respectively, using data of W. M. Thomas, E. H. Gleason and J. J. Pellon, *J. Polymer Sci.*, 17, 275 (1955). [c] Calculated from the data of J. W. Breitenbach and G. Bremer, *Ber.*, 76, 1124 (1943); J. W. Breitenbach and A. Schindler, *Monatsh.*, 83, 271 (1952); and of expt. 64 in Table V. These data show that 0.0329 M benzoyl peroxide is equivalent to 0.0100 M ABN in the polymerization of styrene at 50°. The same ratio is assumed to apply to the polymerization of indene at 50°.

---

(93) G. A. Russell, THIS JOURNAL, 77, 4583 (1955).

double bonds.[16] In the presence of oxygen, the reactive monomer radicals quickly become unreactive peroxide radicals, which react only slowly with unreactive double bonds. The unreactive monomer radicals do not become less reactive by reaction with oxygen. At the other extreme, some monomers polymerize only when oxygen is present. Here, polar and steric effects are involved.

Table XVI summarizes rates of polymerization at 0 and 1 atmosphere of oxygen. The question now arises: what happens to these relations at other pressures? For those polymerizations which are retarded by oxygen, some generalizations can be surmised from Table XVI and from data on styrene (Fig. 1) and methyl methacrylate (Fig. 20). These two systems are probably typical of extreme behaviors. With styrene, the maximum retarding effect of oxygen is realized below one millimeter pressure, with methacrylate at several hundred millimeters. This difference arises because oxygen can compete better with styrene for styrene radicals ($r_1 \simeq 10^{-7}$, equation 25), than with methyl methacrylate for methacrylate radicals ($r_1 = 5 \times 10^{-5}$). Small r_1 values (as for styrene) are probably characteristic of the best electron donors (phenylethylenes and 1,3-dienes) and of monomers with unreactive and unconjugated double bonds. The larger r_1 values are probably characteristic of monomers which are electron acceptors, with conjugated carbonyl, ester and nitrile groups.

The sharp minimum in the rate of polymerization of styrene results from the small value of r_1 and the large value of ϕ (as defined in connection with equation 19), which apparently go together (section 4.1.). For ϕ values of 10–20, styrene would give a broad shallow minimum (Fig. 2). A corresponding effect of crossed termination with methyl methacrylate ($\phi = 20$) is obscured by the larger r_1 value and the steeply rising rate of polymerization at oxygen pressures below 10 mm., where crossed termination is important. The sharp minimum observed experimentally with styrene apparently arises from the very small r_1 and very large ϕ values associated with the change of monomer radicals from $MO_2M\cdot$ (at high pressures) to $MM\cdot$ (at very low pressures). Accordingly, the behaviors of styrene and methyl methacrylate may represent patterns for monomers which are good or poor electron donors, respectively. Other monomers, including most of those with unconjugated double bonds, may have an intermediate behavior: a large retarding effect of very small pressures of oxygen, as with styrene, but a curve without a marked minimum, as with methacrylate.

In summary, the rates of reaction in the presence of oxygen in Table XVI probably apply over a wide range of oxygen pressures. The transition from one limiting rate to the other in the table takes place over a relatively small pressure range, or, in the case of a given initial quantity of oxygen, over a relatively short period of time. The product of reaction changes simultaneously.

In the case of a non-polymerizable unsaturated compound, such as α-methylstyrene, Figs. 9–11 show that, in the low pressure range, the over-all rate of reaction is limited by the oxygen supply. The effect of oxygen on the emulsion polymerization of styrene is considered in section 4.2.

17. Products of Oxidation

17.1. Addition and Transfer Mechanisms.—This section will consider the data in other papers in this group, in Table XV and in the literature, in an effort to correlate olefin structure and products of oxidation. The principal primary products of oxidation of unsaturated compounds below 100° are allylic hydroperoxides, polymeric peroxides, carbonyl compounds formed by cleavage at the double bond, and epoxides. The oxidations considered here are generally chain reactions (*cf.* Table III) which are initiated by reaction 1 and terminated by reaction 7. At low oxygen pressures, termination mechanisms 5 and 6 may be applicable.

There are two principal propagation sequences in oxidation. In reaction 4, a peroxide radical adds to a double bond to give a β-peroxyalkyl radical ($M\cdot$). In reaction 16, the peroxide radical instead removes an allylic hydrogen atom, leaving a substituted allyl radical ($A\cdot$).. In either case, the hydrocarbon radical ($M\cdot$ or $A\cdot$) reacts readily with oxygen to give a new peroxide radical, which continues the chain. Whether the peroxide formed is a polyperoxide or an allylic hydroperoxide depends on the competition between reactions 4 and 16. The discussion below will show that addition reaction 4 is favored whenever the double bond is conjugated with an aromatic, vinyl, carbonyl or nitrile group, or when the unsaturated compound is a 1,1-dialkylethylene. These are the double bonds which are most reactive toward attacking radicals. Compounds with an unreactive double bond, but no reactive hydrogen atoms, such as vinyl acetate, also undergo reaction 4, but with difficulty. Other kinds of unsaturated compounds, with unconjugated and unreactive double bonds, and with reactive hydrogen atoms, undergo reaction 16 at the allylic hydrogen atom. Such oxidations have been reviewed by Bolland[11] and by Bateman.[12] The accompanying cleavage and epoxidation reactions were considered in sections 15.2 and 15.3.

17.2. Polyperoxides.—The following monomers have yielded polymeric peroxides approaching the formula $(MO_2)_n$ when treated with one atmosphere of oxygen at 20–50°: 1,1-diphenylethylene,[94] α-methylstyrene,[46] styrene,[4,26,62] β-methylstyrene (Table XV), indene,[6] methyl methacrylate,[62,95] butyl methacrylate,[96] methacrylonitrile,[92,97] vinyl acetate,[62] vinylidene chloride,[97a] and the conjugated dienes, cyclopentadiene,[98] cyclohexadiene,[98,99] α-terpinene,[99] α-phellandrene,[99] isoprene,[99] 2,3-di-

---

(94) H. Staudinger, *Ber.*, **58**, 1075 (1952).

(95) G. F. Darletskii and A. A. Bendediktova, *Doklady Akad. Nauk S.S.S.R.*, **88**, 67 (1953), probably obtained methyl methacrylate polyperoxide without recognizing it.

(96) J. Exner and M. Bohdanecký, *C. A.*, **51**, 14620 (1957).

(97) K. C. Smeltz and E. Dyer, THIS JOURNAL, **74**, 623 (1952); S. F. Strause and E. Dyer, *ibid.*, **78**, 136 (1956).

(97a) K. Maumi and O. Shibuya, Japanese Patent 5669 (1953); *C. A.*, **49**, 8330 (1955).

(98) H. Hock and F. Depke, *Chem. Ber.*, **84**, 349 (1951).

(99) K. Bodendorf, *Arch. Pharm.*, **271**, 1 (1933); *Chem. Centr.*, **104I**, 1774 (1933).

methyl-1,3-butadiene[99,102] and some conjugated octadecadienoic esters.[100,101,103] The polyperoxides from the dienes had average molecular weights below 100[98,99,103]; 1000, 1800, 1960 and 5000 have been reported for the peroxides from methyl methacrylate[62] butyl methacrylate[96] and styrene.[26] At least some, and probably all, of these oxidations are accelerated by light or peroxides. Acrylonitrile, methyl vinyl ketone and methyl acrylate yielded only unstable low polymer, along with decomposition, cleavage and oxidation products.[92,97] Although chloroprene[104] reacted readily with oxygen, even at 0°, the peroxide was too unstable to isolate. Table XV shows that conjugation is critical. Both α- and β-methylstyrenes gave polyperoxides; their isomer, allylbenzene, gave hydroperoxide, and at a lower rate.

With the exceptions of vinyl acetate[62] and vinylidene chloride,[97a] all the compounds which are known to give polyperoxides have conjugated double bonds, reactive in addition reactions. Among the compounds which have unconjugated double bonds and which react more readily by addition than by transfer, vinyl acetate[62] gives polyperoxide and cleavage products, but α-diisobutylene[70] gives mostly epoxide. Perhaps epoxide formation from $MO_2M\cdot$ is favored when M is large, and/or repressed by groups like acetoxyl.

17.3. Epoxides and Effects of Oxygen Pressure.—At this time, reaction 8 is the only one required to account for formation of epoxides. This reaction occurs readily with unconjugated aliphatic hydrocarbons, as discussed in section 15.3. In the cases of styrene and α-methylstyrene, the monomer radicals are considerably less reactive. To obtain rearrangement to epoxide, the concentration, or life, of the monomer radicals must be increased by lowering the concentration of oxygen (*cf.* sections 4.6 and 8.4). The best yields may be expected with monomers which prefer addition to transfer of peroxide radicals, which do not polymerize by themselves (to waste monomer), and with which polyperoxide formation is restricted by structure or oxygen pressure.

Effects of oxygen pressure on cleavage and epoxidation have been observed thus far only with styrene and α-methylstyrene and, in each case, they accompany marked effects of pressure on over-all rate of oxidation (Figs. 1 and 9). Both are monomers with unusually reactive double bonds, which, on addition of a free radical, give unusually stable monomer radicals. As pointed out by Bateman,[12] the effects of pressure on oxidation of such compounds may become apparent at relatively high pressures. Since reactions 3 and 4 usually proceed at the same rate

$$k_{po}[M\cdot][O_2] = k_{pm}[MO_2\cdot][M] \qquad (56)$$

an increase in the reactivity of the monomer toward $MO_2\cdot$, *i.e.*, an increase in k_{pm}, must result in a decrease in $[MO_2\cdot]$ and an increase in $[M\cdot]$. Thus, other things being equal, the greater the reactivity of the monomer toward radical attack, the higher will be the pressure at which $[M\cdot]$ remains high enough to have an appreciable life, change the termination mechanism (from 7 to 6) and over-all rate, and make reaction 3 rate-determining. These conclusions apply in a comparison of the oxidations of styrene and α-methylstyrene, which is twice as reactive as styrene (section 18). With α-methylstyrene, at 50°, the effect of reduced oxygen pressure on rate becomes apparent at about 1 atmosphere and termination 6 predominates near 25 mm. pressure. With styrene, the effect of pressure becomes obvious at about 20 mm. pressure and termination 6 predominates near 1 mm. pressure.

17.4. Cleavage Reactions.—Unsaturated compounds can be converted to their oxidative cleavage products by several routes: cleavage accompanying propagation (reaction 11 or 12), or cleavage by depolymerization (reaction 9). The latter reaction requires generation of an alkoxy radical in one of three ways: from a monomer radical by reaction 8, from interaction of two peroxide radicals by reaction 14, or from a peroxide molecule by thermal or photodecomposition. Of all of these routes, only 8 + 9 has been found to be sensitive to oxygen pressure.

The following discussion suggests tentatively how rather scanty data on cleavage in the literature may be correlated with present knowledge of cleavage mechanisms. By analogy with styrene and α-methylstyrene, the following cleavages of compounds with reactive double bonds should be partly sensitive to oxygen pressure (8 + 9) and partly insensitive (11 or 12). Cleavage by decomposition of polyperoxide should be unimportant below 60°, important above 100°. Staudinger[94] reported that the oxidation of 1,1-diphenylethylene gave about twice as much benzophenone and formaldehyde as polyperoxide. Considering the high reactivity of this double bond toward free radicals in copolymerization,[16] this cleavage reaction is probably a primary reaction and perhaps more sensitive to oxygen pressure at one atmosphere than even α-methylstyrene. Tiffeneau[105] reported that substituted styrenes of the structure Ar—CR=CH$_2$, where R is methyl, phenyl or *p*-tolyl, yield formaldehyde on slow oxidation by air. The autoxidation of anethole[106,107] (*p*-propenylanisole) has yielded anisaldehyde, acetaldehyde, the corresponding acids, esters and some other carbonyl compounds. Farmer[108] has noted up to 20% of direct cleavage of 1,4-diphenylbutadiene or sorbic ester accompanying the copolymerization with oxygen. Bateman and Morris[109] have reported the direct formation of benzaldehyde by autoxidation of 1,3-diphenylpropene and of 1-phenyl-1-butene. Oxi-

---

(100) W. Kern and J. Stallman, *Makromol. Chem.*, **7**, 199 (1951).

(101) W. Kern, A. R. Heinz and J. Stallman, *ibid.*, **16**, 21 (1955); W. Kern and A. R. Heinz, *ibid.*, **16**, 81 (1955).

(102) F. K. Kawahara, THIS JOURNAL, **79**, 1447 (1957), reported a complex mixture of products from a 28-day oxidation at 43°. At least some of the products were considered to have come from decomposition of polyperoxide.

(103) W. Kern, A. R. Heinz and D. Höhr, *Makromol. Chem.*, **18–19**, 406 (1956).

(104) W. Kern, H. Jockusch and A. Wolfram, *ibid.*, **3**, 223 (1949).

(105) M. Tiffeneau, *Bull. soc. chim.*, [3] **27**, 1066 (1902).

(106) N. A. Milas, THIS JOURNAL, **52**, 739 (1930).

(107) L. Schulz and W. Treibs, *Ber.*, **77**, 377 (1944).

(108) E. H. Farmer, *Trans. Faraday Soc.*, **42**, 228 (1946).

(109) L. Bateman and A. L. Morris, *ibid.*, **49**, 1026 (1953).

dation of methylstilbenes[110] at room temperature, in the presence of benzoyl peroxide and hydrogen bromide, yielded acetophenone and brominated products.

On the other hand, the reported cleavage products of acrylonitrile, methacrylonitrile, methyl acrylate and methyl vinyl ketone, as observed near one atmosphere pressure of oxygen,[92,97] are probably formed at least partly *via* 14 + 9, as in the case with methyl methacrylate (section 12.1). Since several of these polyperoxides are unstable, this route also probably contributes to cleavage.

17.5. Moloxides.—The monomeric moloxides,[22,94,106,107,108,111,112] have been suggested as the source of cleavage products or of transient catalysis by oxidizing solutions, but usually the evidence is only indirect, except for transannular peroxides. Hock and co-workers have presented evidence for the formation of monomeric cyclic peroxides from α-methylstyrene,[46] β-isopropylstyrene,[46] indene,[113] 1-phenylcyclohexene[114] and 1,1′-dicyclohexenyl.[114] Whether light was used in all these oxidations is not specified. In the first three of these peroxides, the peroxide link is supposed to be part of six-membered rings involving two carbon atoms of a benzene ring and two in the side chain. No such monomeric peroxides were found in this Laboratory in work with α-methylstyrene (sections 7.4 and 8.6), indene,[6] and phenylcyclohexene, all without special illumination.

There is no doubt that cyclic dienes give monomeric transannular peroxides when irradiated in the presence of oxygen.[112,115] A diluent serves to retard polymerization, and a photosensitizer is useful[112] but not always essential.[116] Formation of transannular peroxides is probably not a chain reaction since in some cases the sensitized reaction gives a transannular peroxide and the unsensitized reaction gives an allylic hydroperoxide.[112,117]

18. Co-oxidations

A few mixtures of monomers were oxidized for a study of rates, products and relative reactivities, using procedure C (section 2.2). These experiments were run at 4 atmospheres pressure of oxygen to minimize complications from cleavage, and not until much later was it realized that exact corrections for cleavage would be difficult. Sections A and B of Table XVII show that methyl methacrylate has little or no effect on the formation of acetophenone in the oxidation of α-methylstyrene. The indicated rates in the first two experiments were constant within experimental error over the whole reaction time. Only one ester unit entered the copolymer per 16 methylstyrene units. The fraction of oxygen going into acetophenone and formaldehyde (R_C/R_O, 0.22 at 4 atmospheres, 0.69 at 0.18 atmosphere) was substantially the same as in the oxidation of α-methylstyrene alone (0.20 at 4 and 0.67 at 0.20 atmosphere, in Table VII). On the indications of these experiments, the consumption of each monomer in the other copolymerizations has been taken as that found in the copolymer times the factor, R_O/R_P, *i.e.*, total rate of oxidation divided by rate of formation of polymer, for oxidation of that monomer alone at the same pressure. The factors are in notes *f* and *g* in Table XVII. The net result of using these factors is to increase r_i over the value based only on copolymer composition by roughly the factor used for M_i. Since the reaction prerequisite for cleavage differs for styrenes (reaction 8) and methyl methacrylate (14), the validity in copolymerizations of the corrections employed is open to question. However, there is little reason to question our qualitative conclusions, even if our quantitative conclusions are in error by 5–20%.

Section C of Table XVII permits calculations of monomer reactivity ratios and ϕ values for copolymerizations of α-methylstyrene and methyl methacrylate. In this application of the copolymerization equations,[16] the methylstyrene ($M_1\cdot$) and methacrylate ($M_2\cdot$) radicals are all assumed to react only with oxygen to give $M_1O_2\cdot$ and $M_2O_2\cdot$ radicals. This assumption is justified by comparison of the observed and theoretical carbon analyses of polyperoxides made from single monomers in Table XVII. The monomer reactivity ratios are here defined as

$$r_1 = \frac{\text{rate constant for } M_1O_2\cdot \text{ and } M_1}{\text{rate constant for } M_1O_2\cdot \text{ and } M_2} \qquad (57)$$

$$r_2 = \frac{\text{rate constant for } M_2O_2\cdot \text{ and } M_2}{\text{rate constant for } M_2O_2\cdot \text{ and } M_1} \qquad (58)$$

The data in section C of Table XVII lead to the values r_1 (for α-methylstyrene peroxide radicals) = 15 ± 2 and r_2 (for methyl methacrylate peroxide radicals) = 0.041 ± 0.001. The errors given correspond to an uncertainty of 0.3% in the carbon analyses of the copolymers. These results show that α-methylstyrene is 15–25 times as reactive as methyl methacrylate toward either peroxide radical. The r_1r_2 product is 0.62, and there is some tendency for the M_1O_2 and M_2O_2 units to alternate in entering the copolymer.

Calculations of ϕ are also presented in Table XVII. In this section 18, all termination is assumed to involve only peroxide radicals which differ essentially only in their penultimate units, $\sim\!O_2\text{-}M_1O_2\cdot$ and $\sim\!O_2M_2O_2\cdot$; ϕ is a measure of the tendency for crossed termination by these two different peroxide radicals, and is defined according to Flory.[15] Table XVII shows that ϕ is in the range 1–2 for α-methylstyrene and methyl methacrylate, indicating no particular tendency for interaction of unlike radicals.[118]

Section D of Table XVII presents data on the co-

---

(110) H. Suzuki, O. Sinamura and T. Ichihashi, *Bull. Chem. Soc. Japan*, **27**, 235 (1954).

(111) S. Medvedev and P. Zeitlin, *Acta Physicochim. U.R.S.S.*, **20**, 3 (1945).

(112) G. O. Schenck, K. G. Kinkel and H. J. Mertens, *Ann.*, **584**, 125 (1953); G. O. Schenck, H. Eggert and W. Denk, *ibid.*, **584**, 177 (1953).

(113) H. Hock, S. Lang and G. Knauel, *Chem. Ber.*, **83**, 227 (1950).

(114) H. Hock and M. Siebert, *ibid.*, **87**, 554 (1954).

(115) C. Dufraisse, "XIV International Congress of Pure and Applied Chemistry," Birkhäuser Verlag, Basle and Stuttgart, 1955, pp. 27–48.

(116) A. Halpern, *J. Am. Pharm. Assn.*, **40**, 68 (1951).

(117) G. O. Schenck, *Naturwissenschaften*, **40**, 205 (1953).

(118) Because R_O for methyl methacrylate alone in Table XVII is significantly less than the value 0.0062 indicated in Fig. 20, calculations based on the latter value are included in parentheses in Table XVII. After correction for decomposition of ABN, the two values of R_O on which calculations are based are 0.00565 (Table XVII) and 0.00634 (Fig. 20) mole/l./hr.

TABLE XVII

CO-OXIDATION OF α-METHYLSTYRENE OR STYRENE (M_1) WITH METHYL METHACRYLATE (M_2) IN PRESENCE OF 0.01 *M* ABN AT 50°

$[M_1]_0$[a] (moles/l.)	$[M_2]_0$[a] (moles/l.)	Reaction time, hr.	R_O[b]	R_P[c]	Feed g.	Polymer g.	C, %, in copolymer	M_1/M_2 in copolymer	φ
A. α-Methylstyrene and methyl methacrylate with 4.0 atm. of oxygen									
4.10	4.10	6	0.085	0.066				15.9[d]	
B. α-Methylstyrene and methyl methacrylate at 1.0 atm. of air									
4.10	4.10	7	0.061	0.019				16.4[e]	
C. α-Methylstyrene and methyl methacrylate at 4.1 atm. of oxygen (3100 ± 50 mm.)									
7.46	0	1.05	0.1273	0.1010	8.94	0.1605	71.9[i]		
1.91	6.75	3.10	.0397	.0317	9.16	.1471	67.5	4.41[f]	0.9 (1.0)
0.211[a]	8.82	19.0	.0084	.00678	9.29	.1808	54.2	0.436[f]	1.4 (2.0)
0	9.08	34.0 (8.0)[118]	.0052 (0.0062)[118]	.0042	9.23	.1908	45.4[j]		
D. Styrene and methyl methacrylate at 4.1 atm. of oxygen (3100 ± 50 mm.)									
8.43	0	3.0	0.0672	0.0653	8.91	0.269	70.9[k]		
3.02	5.82	5.0	.0261	.0245	9.18	.169	66.7	4.94[g]	1.9 (2.1)
0.435[a]	8.60	17.0	.0089	.0077	9.23	.171	55.3	0.615[g]	1.1 (1.6)
E. Styrene (M_1) and α-methylstyrene (M_2) at 4.2 atm. of oxygen (3200 mm.)									
0.885	6.67	1.50	0.0960	0.0771	9.95	0.1943		0.0633[h,l]	6.2

[a] Initial concentrations of monomers at 50°. The average of the initial and final values of M_1 was used for calculations in the two experiments indicated. [b,c] Average rates of [b] total oxidation or [c] polyperoxide formation, in moles/l./hr. The R_O values for the copolymers include the acetophenone, benzaldehyde or methyl pyruvate calculated to have been formed as indicated in notes *f*, *g*, and *h*. For calculations of φ, the stated R_O values in expts. over 6 hr. were further corrected to allow for variation in average [ABN] with reaction time.[9] [d,e] From methoxyl analyses by Clark Microanalytical Laboratory, 1.63%,[d] 1.58%.[e] [f,g,h] For calculation of $-d[M_1]/-d[M_2]$ in the copolymerization equation, the methylstyrene content of the copolymer was multiplied by 1.26, the styrene content by 1.03 and the methyl methacrylate content by 1.23 to allow for monomer reacting with peroxide radicals, then lost by cleavage. The corrected $-d[M_1]/-d[M_2]$ are [f]4.51 and 0.447, [g]4.12 and 0.515, and [h]0.0517. [i,j,k] Theoretical C contents for pure polyperoxides are 71.98, 45.45 and 70.57%, respectively. Copolymer compositions are based on experimental analyses of polyperoxides containing a single monomer. [l] Some of this peroxide was pyrolyzed by quick heating at low pressure and the volatile products were collected in a trap at −78°. The ratio of benzaldehyde to acetophenone in the trap contents is taken as the ratio of $C_8H_8O_2$ to $C_9H_{10}O_2$ units in the polyperoxide.

polymerization of styrene, methyl methacrylate and oxygen. The values of r_1 and r_2 are 7.9 ± 1.0 and 0.078 ± 0.002. The r_1r_2 product is 0.62, the same as with α-methylstyrene. φ is about the same as for α-methylstyrene and methyl methacrylate.

The single copolymerization of α-methylstyrene (M_2) and styrene (M_1) with oxygen, in section E of Table XVII, with the reasonable assumption that there is no tendency for M_1O_2 and M_2O_2 units to alternate in the copolymer, leads to the relation, $r_2 = 1/r_1 = 2.1$. From the three sets of co-oxidations in sections C, D and E, the relative reactivities of α-methylstyrene, styrene and methyl methacrylate monomers are 15:7:1 toward the $MO_2CH_2C(CH_3)(C_6H_5)O_2\cdot$ radical, 17:8:1 toward the $MO_2CH_2CH(C_6H_5)O_2\cdot$ radical, and 24:13:1 toward the $MO_2CH_2C(CH_3)(CO_2CH_3)O_2\cdot$ radical. Thus α-methylstyrene is twice as reactive as styrene toward any of the three radicals, but the spread between methacrylate monomer and the other monomers depends on R in the attacking $RO_2\cdot$, as indicated by the r_1r_2 products. The relative over-all rates of oxidation of the three monomers alone are 22.5:11.9:1 or 20.1:10.6:1, depending on the rate chosen for methyl methacrylate.[118] Since rates of initiation are presumably identical, the ratios, propagation constant/(termination constant)$^{1/2}$, for the individual oxidations are in the same ratio as the average relative reactivities of the three monomers toward the three peroxide radicals. These relations, together with the small φ values, indicate that differences in oxidation rates of single monomers depend mostly on the monomers, and very little on the peroxide radicals or termination constants. Since the relative reactivities of styrene and α-methylstyrene are independent of the attacking peroxide radical, and since these monomers have identical alternation tendencies in co-oxidations with methyl methacrylate, these hydrocarbons apparently differ in resonance effects on the double bonds and on derived radicals, but not in polar effects.

The small effect of termination constants on the rates of oxidation was unexpected, since Russell[119] recently has pointed out a marked difference in rates of chain termination in autoxidations of saturated hydrocarbons. In oxidations of hydrocarbons, RH, chain termination between two $RO_2\cdot$ radicals is much faster when R is a primary or secondary radical than when R is a tertiary radical. When a similar difference did not appear in the co-oxidation of styrene and methyl methacrylate, the co-oxidation of styrene and α-methylstyrene was investigated. From the r_1 and r_2 values indicated above and the rates of oxidations of the single monomers, φ is found to be 6.2. Experimentally, 11.7 mole % of styrene has reduced the rate of oxidation to the rate expected for 52 mole % styrene if the rate were a linear function of mole fraction of styrene. Calculations show[13] that although only 6.33% of the peroxide radicals formed are styrene peroxide radicals, 44% of the termination reactions involve these radicals in conjunction with α-methylstyrene peroxide radicals. These results may be sensitive to experimental error because the

---

(119) G. A. Russell, THIS JOURNAL, 78, 1047 (1956).

three rates involved differ by a factor of less than two. However, if these results support Russell's conclusions, then an explanation for the low ϕ values for styrene and methacrylate is needed.

19. Reactions of Polyperoxides

The thermal and photochemical decompositions of the polyperoxides of styrene[5] and α-methylstyrene (sections 4.4 and 8.3) are at least partly free radical chain reactions leading primarily to formaldehyde and benzaldehyde or acetophenone. Disproportionation of styrene peroxide into α-hydroxyacetophenone, phenylglycol and phenylglyoxal, particularly in the presence of bases,[5] and its reduction to phenylglycol[5] are the other principal reactions.

As far as can be determined from the literature, copolymers of other unsaturated compounds with oxygen fall into the pattern presented for the copolymers of styrene and α-methylstyrene. The peroxides from indene[6] and 1,1-diphenylethylene[94] are most stable, both being crystalline and melting with decomposition at about 130°. Those from acrylonitrile,[97] methyl acrylate,[97] methyl vinyl ketone[92] and chloroprene[104] are least stable, the latter decomposing even at 0°. Peroxides from 2,3-dimethylbutadiene[101] and methyl methacrylate apparently decompose readily near 100°. The principal products of thermal decomposition of the peroxides are the corresponding aldehydes and ketones. In addition to formaldehyde, benzophenone was obtained from 1,1-diphenylethylene,[94] methyl pyruvate from methyl methacrylate,[62] methyl isopropenyl ketone (as polymer) from dimethylbutadiene,[100] pyruvonitrile and formaldehyde from methacrylonitrile,[92] and a complex mixture from acrylonitrile,[92,97] the expected formyl cyanide being unknown. Data on styrene and α-methylstyrene suggest that aldehydes complicate thermal decompositions[5] and that ketones do not (section 8.3). The peroxides can initiate polymerization,[4,5,62] but only inefficiently (section 4.4), and they react poorly in peroxide tests.[26,62,100] Catalytic reductions of polyperoxides have given results ranging from very poor in the cases of isoprene[99] and 2,3-dimethylbutadiene[99] to around 60% glycol with cyclohexadiene,[99] methyl methacrylate[62] and α-methylstyrene (section 7.8), but our results with styrene peroxide[5] suggest that better yields may be obtainable. Zinc and acetic acid have reduced acrylonitrile polyperoxide to hydroxyacetone (or pyruvaldehyde),[92] and methacrylonitrile to the cyanhydrin of hydroxyacetone.[92] Polymeric peroxides are easily and completely reduced by lithium aluminum hydride.[120]

The results of the oxidations of anethole[107] are consistent with the conclusion that oxidation gives both aldehydes and polyperoxide, and that the latter decomposes in the presence of aldehyde in a manner analogous to styrene peroxide.

Variations must be expected in the reactions of polyperoxides. Further, the monomer:oxygen ratio in the copolymers should have a marked effect on chain reactions of the peroxides.

20. Experimental

The co-oxidations were carried out with 10 ml. of monomer according to procedure C in section 2.2. The origins and oxidations of several monomers in Table XV are described below. Except as otherwise noted, these monomers were shaken with 1 atm. of oxygen in a closed apparatus and rates of oxygen absorption were followed up to 5% conversion. Formaldehyde was not determined but is assumed to be formed in quantities equivalent to the other cleavage product.

Eastman practical **acrylonitrile** was dried over calcium chloride and fractionated through a 60-cm. Vigreux column. The middle fraction was used for oxidation. Evaporation of the oxidation mixture gave a gummy, yellow polymer which evolved hydrogen cyanide slowly at room temperature. This polymer is the polyperoxide[97] from its carbon analysis, 41.6% C (calcd. for $C_3H_3NO_2$, 42.3% C). Niacet commercial **vinyl acetate** was dried over calcium chloride and fractionated through an 80-cm. Fenske column. The middle fraction was used for oxidation. The oxidized solution had 50% of the oxidizing power calculated for the oxygen absorbed, determined by warming a sample with potassium iodide in glacial acetic acid for 15–60 min. at 60°. **1,1-Diphenylethylene** was prepared[121] by Dr. J. R. Ladd. A cut boiling sharply at 121° at 4 mm., $n^{20}\mathrm{D}$ 1.6087, was employed. Acrylic and methacrylic esters were obtained from commercial sources, washed free of inhibitor, and fractionally distilled.

Allylbenzene was prepared by Dr. J. R. Ladd.[122] The material used boiled at 157°, $n^{20}\mathrm{D}$ 1.5120, d^{50}_4 0.8683, and was passed through an activated silica gel column before oxidation. At neither 50 nor 85° did the oxidation produce any polymeric materials that could be precipitated by methanol. At 85° the absorption of 0.0168 mole of oxygen (5 mole %) produced 0.0154 mole (93%) of hydroperoxide, measured by reaction with a dilute solution of hydriodic acid in isopropyl alcohol.[123]

β-Methylstyrene (propenylbenzene) was prepared by Dr. J. R. Ladd.[124] The material was rectified through a 45-cm. column packed with glass helices. Distillate with a constant b.p. (106° at 76 mm.) and a constant refractive index ($n^{20}\mathrm{D}$ 1.5480), d^{50}_4 0.8825, was passed through a silica gel column prior to oxidation.

Absorption of 0.0388 mole of oxygen by 0.374 mole of β-methylstyrene produced a polymeric peroxide that could be precipitated by moist methyl alcohol. The copolymer contained 0.925 mole of O_2 per mole of propenylbenzene (from combustion analysis) and burned with sputtering like styrene peroxide. This polymeric peroxide contained a total of 0.0140 mole of oxygen or 36% of the oxygen absorbed. A total of 0.0242 mole of benzaldehyde was found in the oxidized solution, after the precipitation of the polymeric peroxide, as the 2,4-dinitrophenylhydrazone (m.p. 231–233°). The oxidized solution also contained traces of an acid (0.0007 equivalent) and liberated iodine from acidified potassium iodide[123] equivalent to not more than 0.0004 mole of hydroperoxide. The summary Table XV accounts only for the precipitated peroxide and benzaldehyde (and an assumed equivalent of acetaldehyde) because these are equivalent to the oxygen consumed. The acids and soluble peroxides may have come from incidental subsequent oxidation.

β-Bromostyrene (Eastman Kodak Co.) was distilled through a 45-cm. column packed with glass helices. Constant boiling material (112.5–113° at 22 mm., $n^{20}\mathrm{D}$ 1.6082) was used. In a closed system at 50° no decrease in oxygen pressure was observed for six hours in the presence of 0.01 M ABN. No benzaldehyde was produced. Analysis of the gas after oxidation by a mass spectrometer indicated the absence of volatile material other than oxygen.

Acenaphthylene was prepared from acenaphthene by Dr. R. G. Flowers.[125] The material had been crystallized from ethanol and melted at 84–87°. This material may have been contaminated with acenaphthene, since the reported

---

[120] G. A. Russell, THIS JOURNAL, **75**, 5011 (1953).

[121] A. H. Blatt (Editor), "Organic Syntheses," Coll. Vol. I, second edition, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 226.

[122] D. A. Shirley, "Preparation of Organic Intermediates," John Wiley and Sons, Inc., New York, N. Y., 1951, p. 4.

[123] V. R. Kokatnur and M. Jelling, THIS JOURNAL, **63**, 1432 (1941).

[124] D. Gauthier and P. Gauthier, *Bull. soc. chim.*, **53**, 323 (1933).

[125] R. G. Flowers and H. F. Miller, THIS JOURNAL, **69**, 1388 (1947).

melting point is 93°.[126] In 48 hours, 0.10 mole of acenaphthylene in 50 ml. of chlorobenzene solution absorbed 0.005 mole of oxygen in the presence of 0.1 *M* ABN. The products could not be precipitated by methyl alcohol and were not investigated further.

Acknowledgment.—Miss Bess Rickman, Mrs. V. N. Pemberton and Mr. Kyle Griggs assisted materially in the experimental work in papers V-IX. Mr. A. T. Tweedie carried out some preliminary work on the high temperature oxidation of α-methylstyrene and the low pressure oxidation of diisobutylene. Dr. J. R. Ladd prepared several of the compounds used. Dr. P. D. Zemany and Dr. G. P. Schacher carried out the mass spectrographic analyses for oxygen in connection with experiments in Table V. Several members of the Analytical Chemistry Unit at the General Electric Research Laboratory and of the corresponding Section at Stanford Research Institute assisted with analyses and infrared spectra. Dr. J. F. Brown, Jr., and Dr. B. I. Rowland critically reviewed this manuscript and made numerous useful suggestions.

MENLO PARK, CALIFORNIA

---

[126] G. Egloff, "Physical Constants of Hydrocarbons," Vol. IV, Reinhold Publ. Corp., New York, N. Y., 1947, p. 166.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF TEXAS]

Disproportionation of Alkylbenzenes. III. Behavior of *n*-Butyl-α-C^{14}-benzene upon Treatment with Aluminum Chloride. Further Results with Ethyl-β-C^{14}-benzene[1]

BY ROYSTON M. ROBERTS, STANLEY G. BRANDENBERGER[2] AND STELLAKIS G. PANAYIDES

RECEIVED DECEMBER 12, 1957

n-Butyl-α-C^{14}-benzene was synthesized and subjected to treatment with aluminum chloride at 100°. With a catalyst concentration slightly higher than that which gives 31% isotopic rearrangement of *n*-propyl-β-C^{14}-benzene, only 5% isotopic rearrangement of *n*-butyl-α-C^{14}-benzene occurred. Ethyl-β-C^{14}-benzene was subjected to single and repeated treatments with aluminum chloride in the same concentration used with *n*-propyl-β-C^{14}-benzene and found to give a maximum isotopic rearrangement of 8%. The minor extent of these rearrangements, of *n*-propylbenzene to isopropylbenzene, and of *n*-butylbenzene to *sec*-butylbenzene, are compared to the extensive isotopic rearrangement of *n*-propyl-β-C^{14}-benzene in terms of the mechanism proposed for the latter.

In 1954, the disproportionation of *n*-butylbenzene by aluminum chloride at 100° was described.[3] Mass spectroscopic analysis of the recovered monobutylbenzene and infrared analysis of the dibutylbenzene among the products showed that there was no rearrangement of *n*-butyl groups to *sec*-butyl or other isomeric structures. When this paper appeared, we were engaged in a study of the behavior of *n*-propyl-β-C^{14}-benzene upon disproportionation by aluminum chloride under similar conditions. We found that although very little isomerization to isopropylbenzene occurred, up to 31% of isotopic rearrangement to *n*-propyl-α-C^{14}-benzene did take place.[4] It thus became of interest to determine if isotopically labeled *n*-butylbenzene could be shown to undergo a similar isotopic rearrangement. The present paper describes the synthesis of *n*-butyl-α-C^{14}-benzene and the treatment of this compound with aluminum chloride at 100°.

The synthesis of *n*-butyl-α-C^{14}-benzene involved the same sequence of reactions used for *n*-propyl-β-C^{14}-benzene,[4] but the source of the C^{14} was labeled sodium cyanide rather than alkyl halide. The over-all yield from sodium cyanide-C^{14} was 64%. The product was radioassayed in the form of benzoic acid, produced by permanganate oxidation.

$$\begin{tikzcd}
CH_3CH_2CH_2I \arrow[r, "\text{1, NaC}^{14}\text{N, KCN}", "\text{2, H}_2\text{O, NaOH}"'] & CH_3CH_2CH_2C^{14}O_2Na \arrow[d, "C_6H_6", "AlCl_3"'] \\
CH_3CH_2CH_2C^{14}H_2C_6H_5 & CH_3CH_2CH_2C^{14}OC_6H_5 \arrow[l, "Zn(Hg)_x"', "HCl"]
\end{tikzcd}$$

The *n*-butyl-α-C^{14}-benzene was first heated for 3 hours at 100° with the same proportion of aluminum chloride used by Kinney and Hamilton[3] ($AlCl_3/C_4H_9C_6H_5$, mole ratio 0.20). The reaction mixture was decomposed with water and worked up in the usual way, and the benzene, monobutylbenzene and dibutylbenzene fractions were separated by fractional distillation. Oxidation of the monobutylbenzene and dibutylbenzene fractions by permanganate to benzoic and phthalic acids, respectively, and radioassay of these acids showed that less than 1% of the C^{14} had been lost from the α-positions of the side chains.

The isotopic rearrangement of *n*-propyl-β-C^{14}-benzene was found to be strongly dependent on the concentration of catalyst. With a mole ratio of $AlCl_3/C_3H_7C_6H_5 = 0.16$, 13% isotopic rearrangement occurred, while under otherwise identical conditions, except for a mole ratio of $AlCl_3/C_3H_7C_6H_5 = 0.32$, 31% rearrangement occurred. Hence, the disproportionation of *n*-butyl-α-C^{14}-benzene was repeated using a doubled proportion of catalyst ($AlCl_3/C_4H_9C_6H_5$, mole ratio 0.40). A total of three disproportionations were carried out using this proportion of catalyst and hydrocarbon. The degree of isotopic rearrangement calculated from the radioactivity of the benzoic acid produced from the monobutylbenzene fraction from the first two of these disproportionations was 5.0 and 4.3%, respectively. In the third disproportionation, the dibutylbenzene fraction was also oxidized, and the degree of isotopic isomerization indicated by both

---

[1] Taken from the Ph.D. thesis of Stanley George Brandenberger (1956) and the M.A. thesis of Stellakis George Panayides (1957).

[2] Celanese Corporation of America Fellow, 1955–1956.

[3] R. E. Kinney and L. A. Hamilton, THIS JOURNAL, **76**, 786 (1954).

[4] R. M. Roberts and S. G. Brandenberger, *ibid.*, **79**, 5484 (1957).