Gas-Phase and Liquid-Phase Oxidations of Isobutylene and Cyclopentene

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Radical-initiated oxidations of isobutylene in benzene solution at 80 and 147° and several atmospheres of total pressure are compared with gas-phase oxidations at 147 and 197° and 0.1–0.5-atm total pressure. The isobutylene reacts mostly by the addition mechanism and all oxidations give mostly acetone, isobutylene oxide, and a high-boiling residue as primary products. Radical-initiated oxidations of cyclopentene have been investigated at 100°, from 9 M in the neat hydrocarbon to 0.025 M in chlorobenzene and from 0.027 M to 0.056 M in the gas phase. The rates and products of oxidation appear to be similar in the two phases. Gas-phase oxidations have also been carried out at 155° and good material balances obtained. The main primary product from oxidation of cyclopentene appears to be cyclopentenyl hydroperoxide, but this peroxide is less stable than the products from isobutylene or alkanes, and it causes autocatalysis and gives secondary products. The gas-phase decomposition of cyclopentenyl hydroperoxide was studied at 100° and the effects of some additives were determined. The principal product is cyclopentenol, but, in the presence of cyclopentene and oxygen and in many oxidations of cyclopentene, a high-boiling residue is obtained, apparently a secondary product.

Other work from this laboratory has shown that, except for concentration effects, gas-phase and liquid-phase oxidations of isobutane[2] and n-butane[3] are remarkably similar in rates and products. The present paper compares liquid-phase oxidations of isobutylene at 80 and 147° with its gas-phase oxidations at 147 and 197° and compares liquid-phase oxidations of cyclopentene at 100° with its gas-phase oxidations at 100 and 155°. Our findings are discussed in our Summary and Conclusions. The following paper describes liquid-phase oxidations of α-methystyrene above 110° and the nature of the residues obtained in that oxidation.[4]

Gas-Phase Oxidations of Isobutylene at 147° [5a]

Experimental. Most oxidations were initiated by di-*tert*-butyl peroxide and were carried out in a 526-ml Pyrex flask for 2 hr at 147°, using conventional vacuum techniques. An unheated trap of volume 26 ml was connected to the reaction vessel, just above the level of the oil bath, to facilitate collection and determination of the highest boiling oxidation products. Experiments 42 and 43 were carried out in a new flask without the trap. This change in comparison with expt 38 and 39 seems to have decreased oxygen consumption without affecting the yield of acetone.

The following analytical procedure was ultimately adopted. At the end of an oxidation, the residue trap was cooled and filled with liquid nitrogen and the stopcocks from the reaction vessel were opened slowly. The noncondensable gases, O_2, CO, and N_2 (from t-Bu_2N_2), were then pumped off by a Toepler pump. Their volume and pressure were measured and they were then determined by mass spectrometric analysis. The residue trap was then allowed to warm to room temperature, and the most volatile material distilled into the first cold trap in the vacuum train. The residue not volatile at room temperature was weighed by cutting the residue trap off from the reaction flask at about 0.01 mm. The second trap in this train was cooled in liquid nitrogen and the first one was warmed to −125° in a methylcyclohexane slush bath. The pressure increase as the volatile material distilled was followed on a McLeod gauge. When the pressure had decreased to the original value, the condensate in the second trap was warmed to room temperature, measured with the Toepler pump, and subjected to mass spectrometric analysis. Formaldehyde has been found in this fraction, as shown in Table I. The liquids that remain in the first trap were then analyzed by gc after the addition of an exact quantity of benzene as internal standard. Although no formaldehyde has been found in this fraction, some may have polymerized here or elsewhere in the apparatus.

Experiment 37 in Table I is the best of our first oxidations, where the blanks appeared to consume more oxygen, for reasons that are still obscure. This experiment checked well with expt 35 and 36 (not shown), where the analyses are less complete, and is consistent with the blanks 38 and 39 (without isobutylene), which illustrate the reproducibility of our experiments. In expt 35–37, the total pressures decreased by about 2 mm during reaction, very close to the change calculated from the analyses.

Hydroperoxide was estimated in expt 35 by iodometric titration of the condensable liquids,[6] which were washed from the trap with isopropyl alcohol, the solvent used for the titration. No attempt was made to identify the hydroperoxide, which was obtained in 8.4% yield on the oxygen consumed.

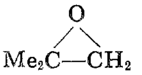
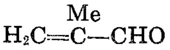
From the work of Batt and Benson,[7] the first-order rate constant for decomposition of t-Bu_2O_2 at 147° is 1.35×10^{-4}/sec, and 62.2% of it should decompose in 2.0 hr. The data in Table I show that the experimental fractions decomposed fall in the satisfactory range of 62–66% in five out of seven listed experiments.

Results. The most useful of our many experiments (many with less complete analyses) are summarized in Table I. The numbers indicate the order in which experiments were carried out. These results show that, although successive experiments would check fairly well, there were some abrupt and significant shifts in results that we are unable to account for. Thus, the blank experiments, 38, 39, 42, and 43, show similar rates of decomposition of t-Bu_2O_2 and similar yields of acetone but different absorptions of oxygen and productions of carbon oxides. Experiment 13 (not shown because of incomplete analyses) should have been entirely comparable to these blanks, but it gave a quantitative yield of acetone, as expected from the work of Raley, *et al.*,[8] for the same rate of disappearance of peroxide.

If any *tert*-butyl alcohol was formed it was not resolved from the methanol by gc. Very little is expected because so many of the *tert*-butoxy radicals cleave in the gas phase at 150°.[2] Further, the 73–88% yields of acetone in the blanks limit the yields of *tert*-butyl alcohol to 27 to 12% and there is never enough methanol and other one-carbon compounds to match the acetone.

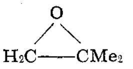
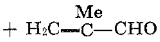
Table II summarizes the products of oxidation of isobutylene, calculated in the following way. The products of oxidations 37, 45, and 40 at 147° are approximated by subtracting from the total reaction products those that are formed in the blanks with peroxide but without isobutylene, adjusting the blanks slightly and proportionately so that the same amount of t-Bu_2O_2 is decomposed in the blank as in the corresponding oxidation.[9] All the results are then expressed in terms of 1 mol of isobutylene reacting. The isobutylene accounted for is the sum of the acetone, isobutylene oxide, methacrolein, and residue. On this basis, essentially all the isobutylene is accounted for in expt 37 and 40 but only 78% in 45, which is not very consistent with the blank. However, it appears that about one-half to three-fourths of a molecule of isobutylene is oxidized per initiating *tert*-butoxy radical regardless of the initial concentration of isobutylene. Of the isobutylene

Table I
Gas-Phase Oxidations of Isobutylene for 2 Hr at 147° [a]

Expt no.	38	39	37	45	42	43	40	46[a]	47[a]
Reactants									
i-C_4H_8	0	0	65.2	65.2	0	0	16.8	0	15.2
O_2	16.8	16.8	16.28	16.8	15.6	15.6	16.8	14.3	15.2
t-Bu_2O_2	2.68	2.68	2.68	2.68	2.47	2.47	2.68	2.29[a]	2.43[a]
Initial pressure, Torr	89	89	397	391	90	89	165.5	90	165.5
Change			−2	−2	+11	+13	+5.5	+8	+3.5
Reactants consumed									
i-C_4H_8	0	0	2.51	1.5	0	0	1.2	0	1.63
O_2	1.84	2.14	5.55	4.53	1.21	1.6	3.42	1.45	3.62
t-Bu_2O_2	1.77	1.68	1.69	1.56	1.57	1.74	1.76	1.35[a]	1.32[a]
Products									
Acetone	2.58	2.60	3.37	2.56	2.79	2.62	3.32	0.75	1.28
MeOH (+ t-BuOH)	1.04	1.26	1.48	0.98	1.24	1.29	1.48	0.99	0.99
CH_2O				Trace		0.35		0.02	0.01
CO	0.48	0.58	0.64	0.28	0.32	0.31	0.46	0.15	0.32
CO_2	0.14		0.71	0.23		0.05	0.26[d]	0.06	0.17
 $Me_2\overset{O}{C{-}CH_2}$	0	0	0.68	0.49	0	0	0.33	0	0.30
 $H_2C{=}\overset{Me}{C}{-}CHO$	0	0	0.2	0.2	0	0	0.1	0	0
RO_2H			0.46[c]						
Residue[b]	0	0	0.80	0.46	0	0	0.35[d]	0	0.23

[a] Quantities are in moles × 10^4. Experiments 46 and 47 used t-Bu_2N_2 instead of t-Bu_2O_2 and were run for 30 min at 197°. Isobutylene and N_2 were also formed (see text). [b] Estimated (C in residue)/4; see text. [c] Result is not available; figure comes from the very similar expt 35. [d] Result is not available; figure is from duplicate run, corrected to same amount of i-C_4H_8 reacting.

Table II
Net Reactions in Gas-Phase Oxidations of Isobutylene at 147 and 197° [a]

	Quantities in moles/mole of i-C_4H_8									
Expt. no.	i-C_4H_8 +	O_2 →	AcMe +	CH_2O +	MeOH +	 $H_2\overset{O}{C{-}C}Me_2$ +	 $H_2C{=}\overset{Me}{C}{-}CHO$ +	residue[b] +	CO +	CO_2
37 − 39[c]	1	1.36	0.31		0.09	0.27	0.08	0.32	0.02$_4$	0.21
45 − (42 43)[d]	1	2.10	0.01		−0.14	0.33	0.13	0.31	0.01	0.14
40 − (42 43)[e]	1	1.56	0.37		0.11	0.27	0.08	0.29	0.11	0.20
47 − 46[f]	1	1.35	0.34	0.19	0.01	0.18	0	0.14	0.10	0.07

[a] Results of oxidation of i-C_4H_8 are corrected by subtracting results of indicated blank without i-C_4H_8, correcting proportionately the products from the blank so that the same amount of initiator was decomposed in the oxidation and the blank. In two instances, the blank is taken as the average of expt 42 and 43. [b] (Gram-atom C)/4. [c] Early experiment with high [i-C_4H_8] at 147°. [d] Late experiment with high [i-C_4H_8] at 147°. [e] Intermediate experiment with low [i-C_4H_8] at 147°. [f] 197° experiment with low [i-C_4H_8].

brought into reaction, about one-third appears as acetone (and presumably formaldehyde and its oxidation product, CO), a little less as isobutylene oxide and residue. Methacrolein is a minor product.

Residues of Gas-Phase Oxidations of Isobutylene at 147°. Several large-scale runs were made to obtain material for investigation. These products had essentially the same infrared spectrum as the residues from experiments in Table I. One residue contained 52.31% C, 9.05% H, and 38.64% O by difference, and had an average molecular weight of 145, corresponding to the average empirical formula $(C_4H_{8.25}O_{2.22})_{1.58}$. Another residue was distilled at about 100° (1 Torr) to yield a distillate containing 50.6% C, 8.7% H, and 40.7% O by difference and having an average molecular weight of 229, corresponding to the average empirical formula $(C_4H_{8.21}O_{2.41})_{2.41}$. The higher molecular weight corresponds to better removal of volatile materials. Note that the indicated H:C ratios are slightly higher than in isobutylene starting material, suggesting the presence of *tert*-butoxy or methyl groups from the initiator.

Gas-phase chromatography indicated the presence of many components but only two major high-boiling components. There was no certainty either that all the sample had eluted or that the residue had not decomposed in the injection block (~160°). Thin layer chromatography on alumina with benzene containing 10% methanol showed considerable streaking but again showed two major components.

The nmr spectrum in CCl_4 solution was complicated. Methyl protons in four different environments were present and there was no splitting of the peaks, indicating the absence of protons on adjacent carbons. The position of the methylene protons in the spectrum showed that they were probably close to oxygen functions. Hydroxyl and aldehyde protons were found and there was also the possibility of vinyl protons. A rough estimate of the numbers of different types of protons is shown in Table III. The combined residues distilled at ~0.1 Torr, and attempts were made to split them into fractions of different volatility. All samples have similar ir spectra, but molecular weight determinations have given values ranging from 150 to 725.

The possibility that this residue was a polymer of methacrolein was investigated. Mixtures of methacrolein vapor, isobutylene, and oxygen were kept in the reaction vessel at 147° for 2 hr and a somewhat similar residue was isolated (identified by infrared). In this case it seems that the methacrolein initiates the oxidation, as no residue was found with methacrolein alone or admixed with either isobutylene or oxygen separately. Methacrolein was polymerized in the vapor phase with di-*tert*-butyl peroxide as initiator at 147°, and the infrared spectrum of the product

Table III
Nmr Investigation of High-Boiling Residue

Type of proton	Relative numbers H atoms	 Groups
Methyl (four types)	18	6
Methylene	~6	3
Hydroxyl	4	4
Aldehyde	1	1
(Vinyl)	4	2

Table IV
Liquid-Phase Oxidations of Isobutylene in Benzene Solution at 147 ± 3°

Expt no. Time, min	L4 95 ± 5	L5 95 ± 5	L6 50 ± 5
Reactants, mmol			
Isobutylene	30.9	31.2	36.0
t-Bu_2O_2	0.075	0	0
Benzene	81.0	84.2	82.9
Oxygen, psi[a]	22.5–36.5 (225.5)	28–47 (222)	179–210 (240)
Products, mmol			
O_2 consumed[b]	~7.2	8.6	8.9
O_2 accounted for[c]	5.5 + 3.1	5.5 + 7	6.6 + 3.7
i-C_4H_8 accounted for[c]	8.9	9.6	10.1
Acetone	4.2–0.08[d]	4.2	5.9
Isobutylene oxide	2.6	2.5	1.3
Hydroperoxides[e]	0.05	0.07	0.07
Residue	8.7[f]	12.7[g]	11.7[h]

[a] Estimated partial pressures of oxygen in excess of the calculated vapor pressures of isobutylene and benzene (in parentheses). For these calculations the vapor pressures of pure isobutylene and benzene are taken as 82.5 and 600 psi, respectively, and their partial pressures in mixtures are taken as proportional to their mole fractions. The gauge pressures were 15 psi less than the indicated total pressures. [b] By pressure decrease in reservoir. [c] First figure for O_2 includes O in acetone, the assumed formaldehyde, and epoxide; second is oxygen in whole residue based on O content of less volatile fraction. Figure for i-C_4H_8 is sum of acetone, epoxide and (gram-atoms of C in residue)/4. [d] 0.08 mmol of acetone is calculated to have arisen from decomposition of 0.042 mmol of t-Bu_2O_2. [e] By iodometric titration. [f] Distillation at 10 Torr pressure gave 48 mg, bp 85–90°, and 182 mg of less volatile material, 45.3% C, 10.4% H, 44.3% O by difference, mol wt 233, corresponding to $C_{8.73}H_{24.0}O_{6.46}$. [g] Residue from distillation to 120° (1 atm) absorbed 0.24 mmol of H_2 on a rhodium on alumina catalyst. For calculations, it is assumed to have the same analysis as the residue in expt L6. [h] Distillation at 15 mm pressure gave 112 mg, bp 95–115°, and 174 mg of less volatile material, 48.9% C, 9.37% H, 41.73% O by difference, mol wt 229, corresponding to $C_{9.32}H_{21.3}O_{5.97}$.

was similar to that of the residue formed in the oxidation. However, the H:C ratios in our residues, 2:1, preclude much contribution from polymer or oxidation products of methacrolein, C_4H_6O.

Gas-Phase Oxidations of Isobutylene at 197° [5a]

Because of the slight reaction of isobutylene with oxygen at 147°, expt 46 and 47 were carried out at 197°. The results, summarized in Tables I and II, indicate that the products and yields per initiating radical are about the same at 197° as at 147°.

In these experiments, 2,2′-azoisobutane was used as initiator. It was prepared from *tert*-butylamine by the procedure of Boozer and Moncrief.[10] Its rate of gas-phase decomposition agreed well with that reported by Levy and Copeland.[11] The thermal decomposition of azoisobutane in oxygen (expt 46, Table I) gave acetone, CO, and CO_2, and also 1.10×10^{-4} mol of nitrogen and 0.70×10^{-4} mol of isobutylene, for which corrections were made in expt 47, Table II.

Oxidations of Isobutylene in Benzene Solution at 147° [5a]

Experimental. Oxidations were carried out in a glass liner of 23-ml capacity in a heated stainless steel rocker bomb, with interior temperatures measured by an iron–constantan thermocouple. Oxygen consumption was measured from the pressure drop in a calibrated reservoir. Reaction mixtures contained the indicated amounts of isobutylene (measured as the cold liquid) and di-*tert*-butyl peroxide in a total volume of 10 ml of benzene solution. Each mixture was placed in the glass liner and the bomb was quickly assembled. Oxygen pressure about 100 psi above the expected vapor pressure was applied and the bomb was rocked at 147 ± 3° for 95 ± 3 min. The bomb was then cooled to room temperature and a sample of the remaining gas was taken for mass spectrometric analysis. The liquid products were analyzed by gc and distillation. The small volume of solution, the high oxygen pressure, and the 95-min reaction time assure an adequate supply of oxygen in solution.

A blank experiment with t-Bu_2O_2 and oxygen but without isobutylene showed no perceptible absorption of oxygen and only the expected traces of acetone from decomposition of the peroxide. Thus benzene appears to be a suitably inert solvent.

Results. Table IV shows that oxidations of isobutylene in benzene solution are about as fast in the absence as in the presence of t-Bu_2O_2. Thus the reaction is self-initiating and we know nothing about kinetic chain lengths. At the higher oxygen pressure, without t-Bu_2O_2, the consumptions of isobutylene and oxygen are higher in 50 min than in 95 min at lower pressure. In expt L4 and L5 at about 2 atm of oxygen, the products are about 45% acetone, 28% isobutylene oxide, and 26% residue on the isobutylene consumed. These are all products of the addition mechanism of oxidation.[12a] Products of the abstraction mechanism, methacrolein and methallyl hydroperoxide, were missing or almost negligible. The acetone/epoxide ratio is higher at higher oxygen pressure, as expected.[13] The H:C ratio in the residue L4 is implausibly high, 2.73 being considerably higher than in isobutylene. The H:C ratio in residue L6 is 2.3, also high but comparable to those in gas-phase residues. We conclude that the stated analysis for L6, at least, is probably too low in carbon and too high in oxygen.

Oxidations of Cyclopentene[5b]

The major primary product of oxidation of cyclopentene is cyclopentenyl hydroperoxide, but the instability of this compound under oxidation conditions has resulted in severe analytical difficulties and in experimental data that are below our usual standard. Our results on cyclopentene are therefore presented as supplementary material (see paragraph at end of paper). However, the qualitative results are clear and our conclusions and a comparison with isobutylene appear below.

Summary and Conclusions

This work preceded most of our work on liquid-phase and gas-phase oxidations of isobutane[2] and n-butane[3] and presented more difficult problems before we had acquired later experience. Difficulties with cyclopentene were more serious; the major primary product is the allylic hydroperoxide. The instability of this peroxide is demonstrated by the autocatalysis in the oxidation of cyclopentene at 50°, established since this work was completed.[12b] Our rates of initiated oxidations at higher temperatures are therefore suspect. In our gas-phase decompositions of cyclopentenyl hydroperoxide at 100°, 30–40% was found to decompose in 8 hr. The major product of the decomposition is cyclopentenol, but with added cyclopentene and oxygen, considerable high-boiling residue was found.

Table V
Summary of Oxidations of Isobutylene at 80–197°

Medium	Benzene solution		Gas phase	
Expt no.	Ref 14	L4	37 − 39	47 − 46
Temp., °C	80	147	147	197
$[i\text{-}C_4H_8]_0$, *M*	~3.3	<3[a]	0.012	0.0027
Conversion, mol %	4	29	4	11
Products, %				
RO_2H	7.7[b]	0.6	(16[c])	
Methacrolein	10.3	~0	8	0
Acetone	18.6	46	31	34
Isobutylene oxide	24.2[d]	29	27	18
Residue	40.7	25	32	14
Residue composition[e]	$C_4H_7O_{1.6}$	$C_4H_{11}O_3$[e]	$C_4H_{8.2}O_{2.2}$	
Addition mechanism, %	81	~99	76	70–100

[a] Concentration of $i\text{-}C_4H_8$ in cold solution was ~3 *M*. [b] 2.7%, mostly methallyl hydroperoxide, in volatile fraction, 5.0% in residue. [c] In residue, included in yield of residue. [d] Includes 1.6% isobutylene glycol and 0.3% of its monoformate. [e] Average composition as four-carbon units; analysis of L4 is probably low in C, high in O.

Isobutylene reacts mostly by the addition mechansim to give saturated and more stable products; these data are more easily interpreted even if some of the products have a fairly high molecular weight. However, the expected minor products of the abstraction mechanism were often undetected at 147 and 197°.

Because of autocatalysis with the alkenes, we still do not have a quantitative comparison of rates of liquid-phase and gas-phase oxidations at the same concentration and temperature. With cyclopentene at 100°, the apparent $k_p/(2k_t)^{1/2}$ in chlorobenzene solution was found to be about four times that in the gas phase; we think that autocatalysis was small but significant. With isobutylene at 80°, autocatalysis was insignificant;[14] at 147°, autocatalysis was overwhelming. We have some good-looking rate and product data on gas-phase oxidations of cyclopentene at 155°, but the probability of autocatalysis makes them quantitatively suspect.

Isobutylene gives substantial proportions of high-boiling residue under all conditions that we have investigated.[14] This result appears to be associated with formation of polyperoxides and the addition mechanism.[4] The nature of this residue[14] is indicated below. However, cyclopentene reacts mostly by the abstraction mechanism and gives *only a little dimeric peroxide residue under conditions* where the products are stable.[12a] The higher proportions of residues in some experiments in this paper appear to be associated with secondary reactions of the hydroperoxide.

In our gas-phase oxidations of both alkenes below 1 atm pressure, there is little chain reaction and much of the involvement of alkene is due to the initiating radicals or their reaction products. The products from isobutylene, like those from α-methylstyrene in the liquid phase,[4] are unexpectedly high in hydrogen content, apparently owing to incorporation of methyl radicals from the initiator in the former instance and of formaldehyde from oxidation in the latter.

We now use the new data above on oxidations of isobutylene at 147 and 197° and previously published data[14] in benzene solution at 80°, all summarized in Table V, to consider the effects of phase change and temperature on the oxidation of isobutylene. We start with previously published results[14] in benzene solution at 80°. Here at least 18% of the isobutylene consumed is supposed to react by the hydrogen abstraction mechanism to give methallyl hydroperoxide, its decomposition product, methacrolein, and hydroperoxide groups in the residue. At least 81% reacts by the addition mechanism, to give mostly residue, and less isobutylene oxide and acetone. The residue consists mostly of C_4 units, joined together by peroxide or ether groups or by polymerization and condensation reactions of saturated and unsaturated aldehydes, but contains some alcohol and hydroperoxide groups associated with the hydrogen-abstraction mechanism.[14]

In a similar experiment at 147°, the oxidation becomes self-initiating and much faster. The yield of acetone increases, mostly at the expense of residue, but 25% of the latter is still found. This shift could be due to greater pyrolysis of polyperoxide groups, either during chain propagation or in secondary reactions. The obvious products of the abstraction mechanism (methallyl hydroperoxide and methacrolein) were not found, probably because they do not survive at the higher temperature and conversions used. Kinetic chain lengths must be fairly long at both temperatures, with considerable propagation by addition of peroxy radicals to double bonds, as shown in the yields of both acetone and epoxide.

In the gas phase at 147° the concentrations of both alkene and oxygen are much lower and the oxidations are much slower. Experiments 37 and 40 (Table I) show that less than one molecule of isobutylene is consumed per potential initiating radical. By hydroperoxide titration, which may measure both primary and secondary products, about half the residue comes from each of the addition and abstraction mechanisms. On this basis, the total contribution of the abstraction mechanism is 24%, somewhat more than the 18% in benzene solution at 80°. Since acetone, but little or no *tert*-butyl alcohol, is formed in the blanks in Table I, *t*-BuO· radicals from the $t\text{-}Bu_2O_2$ initiator must cleave, and most of the gas-phase attack of isobutylene must come from attack by methylperoxy and methoxy radicals. From product analyses, most of these radicals added to isobutylene, although alkoxy radicals are supposed to have more preference for abstraction than alkylperoxy radicals.[15,16] The high H:C ratios in the residues also point to incorporation of methyl radicals. Our experiments tell us little about any simple repeating chain process in the gas-phase oxidation of isobutylene; such processes require considerably higher concentrations (pressures) of reactants, as shown in gas- and liquid-phase oxidations of isobutane[2] and *n*-butane.[3]

The gas-phase oxidation at 197° is faster than at 147°, but the material balance is not adequate to tell us much about the competition between addition and abstraction mechanisms. Here the initiator produces *tert*-butyl radicals, which are oxidized to more isobutylene, which is probably brought into reaction by $t\text{-}BuO_2\cdot$, $MeO_2\cdot$, and MeO· radicals. Comparison of expt 40 and 47 (at the same concentrations, Table I) shows that each initiating radical brings only 0.62 molecule of isobutylene into the reaction at 197°, and only 0.34 at 147°. This small increase in reactivity for a 50° temperature change and the higher yield of abstraction products in the 147° gas-phase run than in the 147° liquid-phase run are consistent with the increasing tendency of radical–alkene addition products to dissociate at high temperatures and low concentrations and to be superseded by abstraction reactions.[17]

The initial products of the gas-phase oxidation of isobutylene at 293° in clean Pyrex are 80% acetone (and formaldehyde + CO), 17% isobutylene oxide, and methacrolein.[18] In an unpacked quartz reactor at 400–550°, a 60% yield of methacrolein has been reported.[19] Together, these results illustrate again the tendency of higher temperatures to cause more reaction by the abstraction mechanism. However, wall reactions[18] have a still undetermined effect on these high temperature oxidations. That the addition/abstraction ratios are not consistent with our own below 200° may also be due to replacement of alkylperoxy radicals by some other, undetermined, chain carrier at high temperatures.

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Registry No.—Isobutylene, 115-11-7; cyclopentene, 142-29-0.

Supplementary Material Available. Full discussion and experimental data for our oxidations of cyclopentene and the decomposition of cyclopentenyl hydroperoxide will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N. W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number JOC-74-885.

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Oxidations of α-Methylstyrene at 110–160°

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This paper considers the transition between the previously reported oxidations of α-methylstyrene[1] at 50 and 170°, with special attention to the nature of the nonvolatile residue, which changes from an alternating copolymer of α-methylstyrene and oxygen to a very complex mixture. Increasing reaction temperature and rate of oxidation result in lower effective oxygen concentrations, formation of increasing ratios of α-methylstyrene oxide to acetophenone, rapidly decreasing formation of polyperoxide above 100°, increasing involvement of primary products in secondary reactions, and gradual replacements of peroxide groups by ether groups, including $-OCH_2O-$ groups, in the residue. The residues average about two α-methylstyrene units, one ether link, and one hydroxy group per molecule, but contain some vinylidene groups. However, vigorous reduction with HI and red P and then with $LiAlH_4$ gives alkylbenzenes with one to four aliphatic carbon atoms and various dimers of α-methylstyrene.

Previous work[1] on the oxidation of α-methylstyrene showed that the principal products at 50° are a polyperoxide, acetophenone, formaldehyde, and α-methylstyrene oxide. The principal chain propagation steps are shown in eq 1–7.

The competition among these reactions largely determines the products of reaction. Alternation of reactions 1 and 2 produces a polymeric peroxide radical that is stabilized as a polyperoxide molecule by some chain transfer step (not yet established but reaction 3 is suggested). Competition between reactions 2 and 4 depends on oxygen pressure and determines how much acetophenone and epoxide are formed. Whenever reaction 4 occurs, the resulting alkoxy radical (which may contain several alternating C_9H_{10} and O_2 units) "unzips" through all the adjacent polyperoxide groups to give acetophenone, formaldehyde, and a small terminal radical (reaction 5). The ratio of carbonyl compounds to epoxide depends on how many times reaction 2 occurs before reaction 4 occurs. The ratio of polyperoxide to smaller molecules depends on the competition between reactions 3 and 4, the former apparently being independent of oxygen and methylstyrene concen-