Oxidation of 2,4,6-Trimethylheptane

Dale E. Van Sickle

Research Laboratories, Tennessee Eastman Company,
Division of Eastman Kodak Company, Kingsport, Tennessee 37662

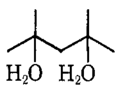
Received July 27, 1971

2,4,6-Trimethylheptane (TMH), a model compound for polypropylene, was autoxidized at 100 and 120°; the kinetic behavior of the reaction was studied, and the major products of the reaction were identified. The synthesis of alcohols, formed as oxidation products (after reduction of the primary product hydroperoxides), is also described. Intramolecular propagation seems to be the dominant reaction pathway in TMH oxidation. The yield of the major product, 2,4,6-trimethyl-2,4,6-heptanetriyl trihydroperoxide, was never greater than ~80% and decreased markedly with increased conversion. At the higher conversions, fragmentation of the hydrocarbon skeleton evidently occurred to give lower molecular weight products which were not identified in the gas chromatographic analysis. Thus, oxygen balances became progressively poorer at higher conversions.

One approach to the study of polymer reactions is the study of model compound reactions. The low-molecular-weight products from the model compound reactions can be isolated and identified in a straightforward manner, whereas identification of products from polymer reactions must be done mainly by spectroscopy.

In polypropylene, the alternate placement of methyl groups along the polymer chain seems to impart special susceptibility to autoxidation. This placement then give a sequence of tertiary hydrogens down the polymer chain adjacent to the methylene group in each repeating unit. A model compound which duplicates this hydrogen sequence in a limited way is 2,4,6-trimethylheptane (TMH). The oxidation of TMH has been reported,[1] but the products were not identified. A more recent article[2] mentioned oxidation of 2,4,6-trimethylnonane but gave no details.

The most relevant works on autoxidation of alkanes containing alternating tertiary hydrogens are by Rust[3] and, more recently, Mill[4] and Montorsi who showed that the principal product of 2,4-dimethylpentane autoxidation is the dihydroperoxide **1**. The ratio of monohydroperoxide **2** to the dihydroperoxide **1** was 1:7, and the combined yields of **1** and **2** accounted for more than 90% of the consumed oxygen. An intermediate step, which is apparently unique to the alternating tertiary center alkanes, involves intramolecular transfer of a hydrogen atom to an alkyl peroxy radical.[4]



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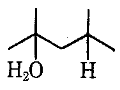

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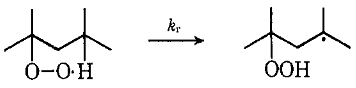
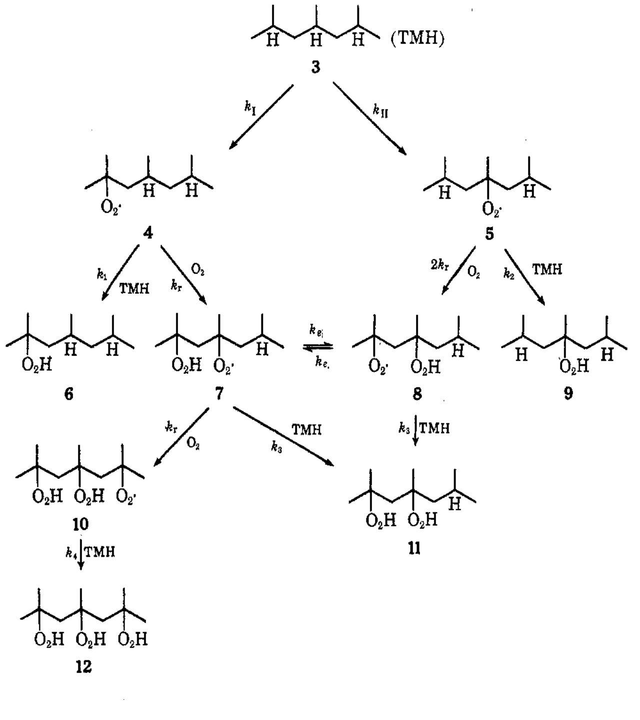


The objective of this research was to determine the generality of intramolecularly propagated oxidation in hydrocarbons by measuring the yields of mono-, di-, and trihydroperoxides formed in the autoxidation of TMH. Sufficient knowledge about the intramolecularly propagated oxidation may suggest whether it is an important propagation step in the autoxidation of polypropylene, where the alternating sequence of tertiary centers is practically infinite.

Results and Discussion

Kinetics of TMH Autoxidation.—This oxidation is apparently too complex to describe with a reasonably concise list of equations. Table I lists the pertinent data obtained, and Scheme I lists the proposed important transformations.

Scheme I



It was assumed that a steady-state concentration of the various peroxy radicals (**4**, **5**, **7**, **8**, and **10**) attack the substrate TMH at the tertiary hydrogens to form alkyl radicals which, after being scavenged by oxygen, are converted to the peroxy radicals **4** and **5**. From this point, a series of competitions occur between intramolecular hydrogen abstraction (rearrangement) (k_r) or intermolecular reaction (k_i, $i = 1, 2, 3, 4$) with more TMH. The final hydroperoxide products are the species **6**, **9**, **11**, **12** which, after triphenylphosphine treatment, give the monohydric alcohols, diols, and triol by glpc analysis.

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[1] A. C. Buchachenko, K. Y. Kaganskaya, and M. B. Nieman, *Kinet. Katal.*, **2**, 38, 149 (1961).

[2] J. C. W. Chien, *J. Phys. Chem.*, **71**, 2247 (1967).

[3] F. Rust, *J. Amer. Chem. Soc.*, **79**, 4000 (1957).

[4] T. Mill and G. Montorsi, Abstracts, 161st National Meeting of the American Chemical Society, March 28, 1971, Petr. No. 8.

TABLE I

RATES AND PRODUCTS OF TRIMETHYLHEPTANE OXIDATION AT 100°

								O$_2$H Yield		Yield of products, mmol^{d}			
Expt no.	TMH, mmol	Soln vol, ml^{a}	[TMH], M	[*tert*-Bu$_2$O$_2$], M	Oxidn rate × 10^{6},^{b} M min^{-1}	O$_2$ consumed, mmol	Time, min	mmol^{c}	O$_2$ consumed, %	Monohydric alcohols^{e}	Diols^{f}	Triol	Other^{g}
34^{h}	124.1	26.3	4.72	0.0085^{i}	44	1.94	1703	1.41	73				
141	104.8	22.9	4.58	0.0066	62	4.22	1370	2.46	58	0.054	0.048	0.25	0.343^{j}
62	100.6	21.9	4.58	0.0091	66	0.97	510	0.79	81	0.023	0.022	0.137	0.11
138	109.1	23.7	4.58	0.0102	72	1.01	505	0.77	77	0.01	0.019	0.076	0.07^{k}
105	108.5	23.7	4.58	0.0280	96	1.37	465	0.96	70	0.019	0.026	0.158	0.11
111	106.3	23.3	4.58	0.0607	142	1.28	365	0.94	73	0.018	0.024	0.15	0.13
147^{l}	110.7	24.8	4.46	0.0000	193	1.48	150	1.02	69				
59^{l}	98.7	22.1	4.46	0.0142	650	1.23	70	0.91	74	0.024	0.029	0.18	0.18
144^{l}	138.1	39.5	3.50^{m}	0.0119	209	1.72	220	1.14	66				
101^{l}	96.0	41.0	2.30^{m}	0.0108	94	1.49	382	0.76	52	0.022	0.075	0.145	0.19
108^{l}	117.8	80.3	1.46^{m}	0.0109	72	2.18	465	0.98	45	0.01	0.011	0.11	0.11
130^{n}	108.1	23.9	4.57	0.0324	55	1.30	715	0.84^{o}	65	0.11	0.11	0.17	1.83;^{p} 0.13^{g}
133^{q}	88.7	20.8	4.26	0.0404	96	1.40	651	1.09	78	0.02	0.025	0.14	0.26;^{r} 0.06^{g}

[a] At reaction temperature. [b] Initial rate, mol l.$^{-1}$ min^{-1}. [c] Iodometric titration.[5] [d] By glpc after triphenylphosphine reduction. [e] 2,4,6-Trimethyl-2- and -4-heptanols. [f] 2,4,6-Trimethyl-2,4- and, if any, -2,6-heptanediols. [g] Summation of five to ten unidentified peaks, mol wt of 170 assumed. [h] 80°. [i] 1,1′-Azodicyclohexanecarbonitrile (ADC). [j] 0.44 mequiv of acid present (from NaOH titration). [k] 0.012 mequiv of acid present. [l] 120°. [m] Benzene solutions. [n] Tetralin hydroperoxide concentration = 1.675 mol = 0.07 M. [o] Net hydroperoxide formed (total titre = 167 mmol). [p] Tetralone and tetralol found following triphenylphosphine reduction. [q] Cumene concentration = 9.36 mmol = 0.45 M. [r] Cumyl alcohol.

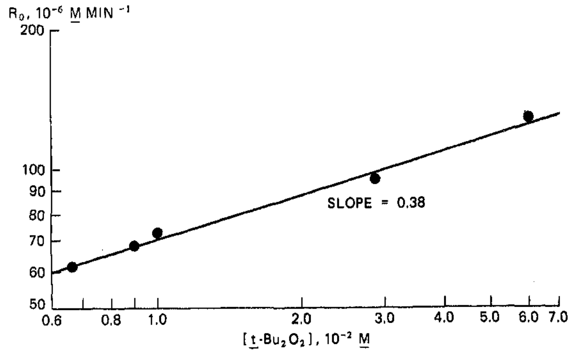

Figure 1.—Oxidation rate dependence on initiation rate.

It was of interest to see whether the oxidation rate dependence conformed to simple rate laws, applicable to many oxidations, where kinetic chain lengths are long, of the form

$$R_o = -dO_2/dt = (R_i/2k_t)^{1/2}k_p[\mathrm{RH}] \qquad (1)$$

where R_o = rate of oxidation, R_i = rate of initiation, k_p = rate constant for propagation, k_t = rate constant for termination, and [RH] = concentration of substrate.[6] Kinetic chain lengths for the TMH oxidations of Table I are estimated to range from 100 to 10. The TMH oxidation system is too complex to make an exact steady-state analysis tractable, but a simple law such as eq 1 might be approximated. For instance, Mill and Montorsi[4] made an analysis of the dimethylpentane system and, with certain simplifying assumptions, obtained an expression for the oxidation rate.

$$R_o = (R_i/2ak_t)^{1/2}k_p[\mathrm{RH}]\left[\frac{k_p'[\mathrm{RH}]}{k_r} + 2\right] + \frac{R_i}{2a}\left[\frac{k_p'[\mathrm{RH}]}{k_r} + {}^1/_2\right] \qquad (2)$$

Both k_p and k_p' are propagation rate constants for the two principal peroxy radicals present and a is the fraction of termination from the reaction of two peroxy radicals. On the assumption that the first term of eq 2 dominates and that $2 \gg k_p'[\mathrm{RH}]/k_r$, eq 2 reduces to eq 3, which is the same as eq 1 except for the factor of 2 (when $a = 1$).

$$R_o = 2(R_i/2ak_t)^{1/2}k_p[\mathrm{RH}] \qquad (3)$$

For TMH the oxidation rate (R_o) dependence on the initiation rate (R_i) was determined by the usual log–log plot of R_o against initiator concentration which is proportional to R_i. The results are shown in Figure 1. There is some scatter in the data but no point lies more than 8–10% from the line which was drawn. The slope of the line is 0.38, significantly lower than the 0.50 expected. The outcome is somewhat surprising, since most oxidations show initiator dependence orders from 0.5 to 1.0.

Orders in initiation rate of $^1/_3$ can be predicted from certain models of oxidation mechanisms, which involve a dominating amount of nonterminating peroxy radical interaction ($a \ll 1$) and subsequent cleavage of the alkoxy radicals formed.

$$2\mathrm{RO_2\cdot} \longrightarrow 2\mathrm{RO\cdot} + \mathrm{O_2}$$

$$\mathrm{RO\cdot} \longrightarrow \mathrm{R'\cdot} + \mathrm{R''{=}O}$$

Although the TMH oxidation to hydroperoxides is far from quantitative, an explanation for the odd initiator dependence lies in the existence of a second source of initiation.

The temperature dependence of the reaction was estimated from experiments 34, 138, and 59 by correcting the initial rates to unit hydrocarbon concentration and unit initiation rate and assuming eq 1 to be valid. Rates of initiation were calculated from eq 4.

$$R_i = 2k_d[tert\text{-}\mathrm{Bu_2O_2}] \qquad (4)$$

The values of k_d used were extrapolations of previously published data.[7,8] The results are summarized in

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[5] R. D. Mair and A. J. Graupner, *Anal. Chem.*, **36**, 194 (1964).

[6] L. Bateman, *Quart. Rev., Chem. Soc.*, **8**, 147 (1954).

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

[8] L. Batt and S. W. Benson, *J. Chem. Phys.*, **30**, 895 (1962).

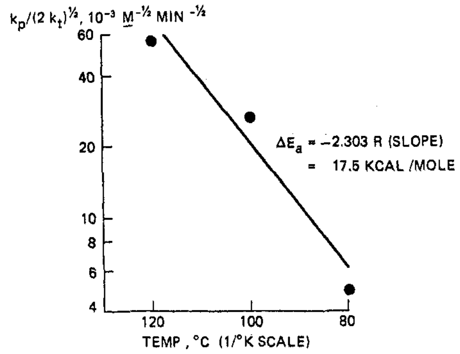

Figure 2.—Temperature dependence of TMH oxidation.

Table II, and the $R_o/R_i^{1/2}$ [TMH] values were subjected to the usual Arrhenius plot (Figure 2). There is some scatter, but the visually determined "best line" has a slope which corresponds to an activation energy of 16.5 kcal/mol, which appears to be too large. Correction of the rates to a 0.38 power dependency in R_i removes most of the scatter (actually curvature), but the line retains the same slope. For the closely related 2,4-dimethylpentane, a value for $E_p - {}^1/_2E_t$ of 10.7 kcal/mol was reported;[3] and for the simplest system, isobutane, the reported value was 12 kcal/mol.[9] For most systems, the value of E_p alone is not higher than 10 kcal/mol.[10] Measurement of the absolute value of the propagation rate constant for TMH at different temperatures indicated a E_p of only 9.1 kcal/mol.[1] It appears that there was a second source of initiation, either a direct thermal initiation or very early hydroperoxide decomposition, which was not accounted for in estimating composite rate constants in Table II.

TABLE II

TEMPERATURE DEPENDENCE OF TMH OXIDATION RATE

Expt no.	Temp, °C	$R_o \times 10^6$, $M\,\mathrm{min}^{-1\,a}$	$R_i \times 10^6$, $M\,\mathrm{min}^{-1\,b}$	[TMH], M	$R_o/R_i^{1/2}$ [TMH]	$R_o/R_i^{0.38}$ [TMH]
34	80	44	5.01	4.72	4.1	9.53
138	100	72	0.76	4.58	18.2	33.1
59	120	650	13.3	4.46	40.0	100.5

[a] From Table I. [b] Calculated from eq 7 (100 and 120°) or $k_d = 2ek'_d$ [ADC] (80°); k_d for *tert*-Bu_2O_2 = 3.66×10^{-5} min^{-1} (100°)[8] and 4.67×10^{-4} min^{-1} (120°);[8] k'_d for ADC = 4.97×10^{-4} min^{-1} (80°).[7]

Experiment 147 with neat TMH and no initiator at 120° indicated that thermal initiation began immediately and that the initiation rate rapidly accelerated with the consumption of oxygen, presumably as a result of hydroperoxide decomposition. Therefore, it seems probable that the earliest measurable rates of the experiments with di-*tert*-butyl peroxide present were enhanced by either thermal initiation or autocatalysis.

The effect of benzene dilution of TMH oxidation mixtures was twofold. First, the apparent initial oxidation rate decreased rapidly when a small amount of benzene was added; then it apparently became proportional to the TMH concentration. A plot of R_o *vs.* TMH concentration is shown in Figure 3. The second effect of benzene dilution of TMH oxidation mixtures was on autocatalysis. In experiment 59, with pure TMH, the oxidation rate accelerated with conversion and the final rate was 50% higher than the initial rate. In experiment 144, where the TMH concentration was reduced by only 21%, no autocatalysis was observed and the final rate equaled the initial rate. The inhibition of autocatalysis by benzene dilution was noted,[7] but not explained. Simple preservation of the hydroperoxide is not the answer, since hydroperoxide yields progressively decreased with increased benzene dilution of the TMH. The reduced hydroperoxide yield may result partly from low kinetic chain lengths at the highest benzene dilutions.

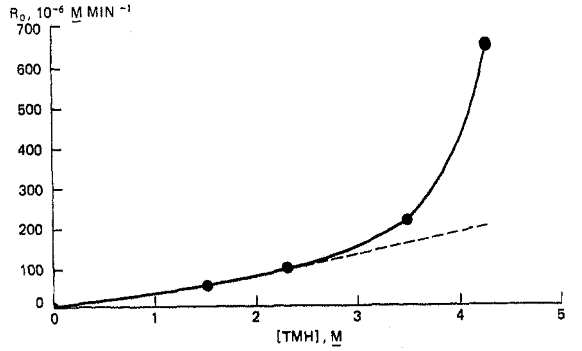

Figure 3.—Hydrocarbon concentration dependence of TMH oxidation.

Products of TMH Oxidation.—It was initially hoped that the oxidation of TMH would be sufficiently similar to that of 2,4-dimethylpentane so that an extension of Mill[4] and Montorsi's kinetic analysis could be used in this study. The difficulties encountered in the product analysis seem to obviate this possibility. First, at no time during the oxidation was the hydroperoxide yield (relative to oxygen absorbed) greater than ~80%. Hydroperoxide yields of 2,4-dimethylpentane oxidations were greater than 90% and were relatively insensitive to conversion (the hydroperoxide yields were nearly 90% at 10–15% conversion).[3] TMH, in contrast, gave the highest hydroperoxide yield at less than 1% conversion and the yield dropped sharply to 58% at 4% conversion. The yield of carboxylic acid rose as per cent conversion rose, which may have been the result of attack on the hydroperoxide or accelerated thermal decomposition.

Another surprising factor was the large preponderance of the trihydroperoxide with only small amounts of mono- and dihydroperoxide present at any time. The relative amounts of mono-, di-, and trihydroperoxide were not appreciably changed by benzene dilution, except that more unidentified side products were formed, perhaps at the expense of the trihydroperoxide.

The most disconcerting part of the product analysis was the amount of alcohols found compared to the amount of hydroperoxide titrated. Thus, for experiment 62, the theoretical amount of hydroperoxide associated with the alcohols found was 3(0.14) + 2(0.02) + 1(0.02) = 0.48 mmol, but the actual amount titrated was 0.79 mmol. For experiment 59, the values were 0.62 mmol (theoretical) *vs.* 0.91 mmol (actual). Before the glpc responses were calibrated, it appeared that alcohol yields satisfactorily matched the hydroperoxide titre, but repeated glpc experiments with weighed alcohols and internal standard (dimethyl succinate) showed that the alcohol shortages were real.

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(9) D. L. Allara, T. Mill, D. G. Hendry, and F. R. Mayo, *Advan. Chem. Ser.*, **76**, 40 (1968).

(10) D. G. Hendry, *J. Amer. Chem. Soc.*, **89**, 5433 (1967).

The triphenylphosphine reduction procedure was changed in experiment 138 to include 1.5 hr of reaction on a steam bath prior to the distillation to concentrate the products. This procedure apparently further reduced the yield of triol relative to titrated hydroperoxide. At this point, one can only speculate that either the triphenylphosphine reduction was inefficient, with some hydroperoxide being converted to products other than the expected alcohols, or the unidentified products of the glpc trace corresponded to hydroperoxidic products with more than one hydroperoxide group per mole of the unidentified materials.

The quantity listed in the "other" column of Table I is an estimation of the material corresponding to the area of approximately 12 peaks in the chromatograph trace. For neat TMH, only one of these unidentified peaks had substantial area (less area than that of the diol). Elution time of this peak was between those of the diol and triol, and its area seemed to increase as product solutions were allowed to stand at room temperature. Whatever the products of the TMH hydroperoxide decomposition were, some apparently were low molecular weight and were obscured by the large peak of unreacted TMH in the glpc analysis.

The last two experiments (130 and 133) of Table I were attempts to change the product ratios by adding an agent more active in transfer than the TMH substrate. Tetralin hydroperoxide (0.07 *M*), which is a very efficient transfer agent for peroxy radicals,[11] did not prevent the trihydroperoxide from becoming the major product of the oxidation, although the relative yields of mono- and dihydroperoxides were increased. Cumene had scarcely any effect on the product ratios, although the amount of cumyl alcohol detected indicated substantial participation of cumene in the oxidation. The experiment with tetralin hydroperoxide resulted in a good balance of the net hydroperoxide formed and the yields of TMH alcohols, but the experiment with cumene again resulted in an alcohol shortage [0.75 mmol of OH (theoretical) *vs.* 1.09 mmol of O_2H (actual)].

From Scheme I and the data of Table I qualitative conclusions can be made regarding the relative values of some of the rate constants involved. In Scheme I, the rate constants k_I and k_{II} include include the sum of the steady-state concentrations of all the peroxy radicals of the system. Since the intention is to form ratios of rates of formation of products, this steady-state sum need not be explicitly determined. Also, it was assumed that the alkyl radicals formed were quickly scavenged by oxygen and did not enter into propagation reactions. Then the steady state equations for the peroxy radical intermediates are as follows.

$$\frac{d[\mathbf{4}]}{dt} = k_I[\mathrm{TMH}] - k_1[\mathbf{4}][\mathrm{TMH}] - k_r[\mathbf{4}] = 0 \qquad (5)$$

$$\frac{d[\mathbf{5}]}{dt} = k_{II}[\mathrm{TMH}] - k_2[\mathbf{5}][\mathrm{TMH}] - 2k_r[\mathbf{5}] = 0 \qquad (6)$$

$$\frac{d[\mathbf{7}]}{dt} = k_e[\mathbf{8}] + k_r[\mathbf{4}] - (k_3[\mathrm{TMH}] + k_r + k_e)[\mathbf{7}] = 0 \qquad (7)$$

$$\frac{d[\mathbf{8}]}{dt} = k_e[\mathbf{7}] + 2k_r[\mathbf{5}] - (k_3[\mathrm{TMH}] + k_e)[\mathbf{8}] = 0 \qquad (8)$$

$$\frac{d[\mathbf{10}]}{dt} = k_r[\mathbf{7}] - k_4[\mathrm{TMH}][\mathbf{10}] = 0 \qquad (9)$$

These five independent equations and five unknowns can be solved directly, but the algebraic expressions become complicated. However, substantial simplification results from the use of the product analyses which indicated $k_4 \gg k_i$ [TMH] (i = 1, 2, 3, 4); that is, intramolecular propagation is favored over intermolecular transfer. The steady state concentrations are

$$[\mathbf{4}] = \frac{k_I[\mathrm{TMH}]}{k_r} \qquad (10)$$

$$[\mathbf{5}] = \frac{k_{II}[\mathrm{TMH}]}{2k_r} \qquad (11)$$

$$[\mathbf{7}] = \frac{k_r[\mathbf{4}] + k_e[\mathbf{8}]}{k_r + k_e} = \frac{(k_{II} + k_I)[\mathrm{TMH}]}{k_r} \qquad (12)$$

$$[\mathbf{8}] = \frac{2k_r[\mathbf{5}] + k_e[\mathbf{7}]}{k_e} = \frac{k_{II}[\mathrm{TMH}]}{k_e} + \frac{(k_{II} + k_I)[\mathrm{TMH}]}{k_r} \qquad (13)$$

$$[\mathbf{10}] = \frac{k_r[\mathbf{7}]}{k_4[\mathrm{TMH}]} = \frac{(k_{II} + k_I)}{k_4} \qquad (14)$$

The rates of diol and triol formation are

$$\frac{d(\mathbf{11})}{dt} = k_3[\mathrm{TMH}]([\mathbf{7}] + [\mathbf{8}]) \qquad (15)$$

$$\frac{d(\mathbf{12})}{dt} = k_4[\mathrm{TMH}][\mathbf{10}] \qquad (16)$$

so that the ratio of their rates of formation is

$$\begin{aligned}\frac{d(\mathbf{11})}{d(\mathbf{12})} &= \frac{k_3([\mathbf{7}] + [\mathbf{8}])}{k_4[\mathbf{10}]} \\ &= \frac{k_3[\mathrm{TMH}]}{(k_I + k_{II})}\left[\frac{2(k_I + k_{II})}{k_r} + \frac{k_{II}}{k_e}\right]\end{aligned} \qquad (17)$$

If it is assumed that $k_I = 2k_{II}$ and that $k_e \gg k_r$ (not an unreasonable assumption based on rates reported for analogous intermolecular processes[12]), then eq 17 becomes

$$\frac{d(\mathbf{11})}{d(\mathbf{12})} = \frac{2k_3[\mathrm{TMH}]}{k_r} \qquad (18)$$

Thus, from the data of experiment 62, a typical value for the ratio of intermolecular to intramolecular propagation would be

$$\frac{k_3}{k_r} = \frac{[d(\mathbf{11})/d(\mathbf{12})]}{2[\mathrm{TMH}]} = \frac{[0.02/0.14]}{(2)(4.6)} = 0.015\,M^{-1} \qquad (19)$$

For 2,4-dimethylpentane, where only one competition exists between intermolecular (k_p) and intramolecular (k_r) propagation, a value of $k_p/k_r = 0.013$ was reported; this is in unexpectedly good agreement with the TMH results. The small difference of the values is in the right direction but of insufficient magnitude to clearly indicate that the dihydroperoxide of TMH maintains high stability relative to the trihydroperoxide. The data of Table I and the reported results for 2,4-dimethylpentane[4] indicate little or no temperature dependence for the k_i/k_r ratios.

Conclusions

Like 2,4-dimethylpentane, TMH preferentially oxidizes by an intramolecular propagation reaction. The intramolecular propagation is, in fact, much faster than the intermolecular transfer reaction, and very reactive transfer agents are required to intercept the intramolecular reaction. (The intramolecular prop-

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[11] K. U. Ingold, *Accounts Chem. Res.*, **2**, 1 (1969).

[12] J. A. Howard, W. J. Schwalm, and K. U. Ingold, *Advan. Chem. Ser.*, **75**, 6 (1967).

agation reaction appears to be general for 1,3,5-methyl substituted alkanes.) These results may be relevant to the polypropylene stabilization problem, where it is necessary to interrupt the intramolecularly propagated oxidation of a 1,3,5. . .substituted polymer chain with an inhibitor. In the viscous polymer system, collisions between inhibitor and polymer are greatly restricted, and it is surprising that low levels of inhibitor are effective.

As the number of intramolecularly situated hydroperoxy groups in the product increase, significant differences in the oxidation system occur. Neat isobutane[9] and 2,4-dimethylpentane[4] oxidize with little or no autocatalysis, and hydroperoxide yields are regularly greater than 90% of consumed oxygen. Neat TMH oxidizes with substantial autocatalysis (at 120°) which is easily inhibited with a small quantity of benzene, and hydroperoxide yields are approximately 70%. Moderately concentrated benzene solutions of polypropylene (up to 3.98 *M* in monomer units) oxidize with some autocatalysis,[13] and the hydroperoxide yield at 1% conversion is ~40%. Apparently the propensity of the hydroperoxides to decompose is related to the number of hydroperoxide groups at adjacent positions and increases significantly as the number of groups in the cluster increases.

Experimental Section

Materials.—2,4,6-Trimethylheptane (99% pure) was purchased from Chemical Samples Co., Columbus, Ohio. It was passed over neutral alumina just prior to use. Eastman reagent grade cumene was carefully fractionated [bp 153° (733.4 mm)] to remove an impurity detected by glpc. Tetralin hydroperoxide was synthesized and purified by a reported procedure.[14] 1,1′-Azodicyclohexanecarbonitrile obtained from Chemical Procurement Laboratories was recrystallized from acetone–methanol. Di-*tert*-butyl peroxide (*tert*-Bu_2O_2) (99% pure) was purchased from Wallace and Tiernan, Inc., Lucidol Div. "Chromatoquality" benzene was purchased from Matheson Coleman and Bell. Eastman reagent grade triphenylphosphine was sublimed before use. 2,4,6-Trimethyl-1,6-heptadien-4-ol was purchased from Chemical Samples Co.

Of the five monohydric alcohols, diols, and triols expected as oxidation products (following reduction[15] of the corresponding hydroperoxides with triphenylphosphine), only the two monohydric alcohols have been described previously. All five alcohols were synthesized for use as glpc standards.

2,4,6-Trimethyl-4-heptanol.—2,4,6-Trimethyl-1,6-heptadien-4-ol (10 g) was hydrogenated at room temperature in 50 ml of ethanol with 1 g of 5% Pd on charcoal catalyst until no more hydrogen was adsorbed. Filtration and distillation of the ethanol solvent left an oil (2,4,6-trimethylheptanol) which distilled at 84° (23 mm) [lit.[16] bp 86–87° (26 mm)]. The nmr spectrum of the product confirmed the proposed structure.

2,4,6-Trimethyl-2-heptanol.—4,6-Dimethyl-2-heptanone [bp 107–108° (101 mm)] was isolated in 97% purity (as measured by glpc) from technical diisobutyl ketone by careful fractionation. The structure of the distillate was confirmed by nmr. The dimethylheptanone (20 g, 0.152 mol) was treated with excess methylmagnesium bromide in diethyl ether. Removal of the ether from the dried product solution left an oil which distilled at 60° (3 mm) [lit.[17] bp 80° (25 mm)]; yield was 18 g (75%). An nmr spectrum confirmed the structure.

2,4,6-Trimethyl-2,4-heptanediol.—This material was synthesized from ethyl 3,5-dimethyl-3-hydroxyhexanoate, which was prepared by a Reformatsky reaction according to the procedure of Surzur.[18] Methyl isopropyl ketone, ethyl bromoacetate, and zinc were treated as described by the procedure[18] to give the hydroxy ester in 52% yield [lit.[18] bp 101° (76 mm)]. The hydroxy ester (20 g, 0.106 mol) was treated with excess methylmagnesium bromide in ether by stirring at reflux overnight. The usual work-up procedure with dilute sulfuric acid afforded an ether solution of product which, after drying and distillation, yielded 8 g (43%) of diol: bp 118–123° (0.5 mm); ir max 3350, 2900–3000, 1470, 1415, 1380, 1185, 1042, 870, and 759 cm^{-1}; nmr ($CDCl_3$) δ 0.9 (d, 6, terminal methyl protons), 1.1–1.5 (m, 11), 1.65 (d, 2, center methylene protons), 4.35 (d, 2, hydroxy protons), and one proton (isopropyl) not resolved.

2,4,6-Trimethyl-2,6-heptanediol.—3-Methylglutaric acid obtained from Columbia Organic Chemical Co. was converted to the diethyl ester, bp 94–95° (3.1 mm). Reaction of 5 g (0.025 mol) of the ester with an excess (~0.3 mol) of methylmagnesium bromide in ether yielded ~5 g of a crude oil. The oil partially crystallized on standing, but could not be distilled without dehydrating to an unsaturated alcohol. No solvent was found which would satisfactorily serve for recrystallization of the crude product, but, after long-term sublimation of the crude product, white crystals were obtained: mp 64–66°; ir max 3240, 2970–2850, 1380, 1367, 1185, 1064, 979, 952, 932, 891, 858, and 774 cm^{-1}; nmr ($CDCl_3$) δ 1.00 (d, 3, center methylene protons), 1.20 (s, 12, terminal methyl protons), 1.3–2.0 (m, 5, secondary and tertiary protons), 3.4 (s, 2, hydroxy protons).

2,4,6-Trimethyl-2,4,6-heptanetriol.—2,6-Dihydroxy-2,6-dimethyl-4-heptanone (5 g, 0.0333 mol) obtained from K & K Laboratories, Inc) was treated with an excess of methylmagnesium bromide in ether by refluxing overnight. Work-up of the reaction mixture was accomplished by the cautious addition of 1 *N* sulfuric acid, followed by continuous ether extraction of the aqueous phase. Concentration of the dried ether solution of products gave a heavy oil (~5 g) which could not be crystallized. Analysis of the oil by glpc (20% silicone SE-30 on Chromosorb P, 6 ft × 0.25 in.) indicated that some of the starting ketone was present, but that a major product (with the longest retention time in the trace) constituted about $^2/_3$ of the total. This major product was isolated by repetitive preparatory glpc in sufficient quantity for spectral analysis and use as an authentic sample of triol to add to product solutions from TMH oxidations: ir max 3350, 2980, 2940, 1470, 1415, 1380, 1192, 1060, 935, 867 and 771 cm^{-1}; nmr ($CDCl_3$) δ 1.2–1.4 (d, 12, terminal methyl protons), 1.43 (s, 3, center methyl protons), 1.73 (m, 4, methylene protons), 5.08 (s, 3, hydroxyl protons).

Oxidation Procedure.—Most of the details of autoxidizing liquid samples have been described.[7] Solutions of the TMH, initiator, and any cooxidant were made in the reaction bulbs. Normally, ~20 ml of solution was prepared in bulbs of ~31 ml capacity. Reaction progress was followed and the rates were calculated as described.[7] After the reaction mixture was cooled, the gas vented, and the bulb detached, 5 ml of propyl acetate was added to redissolve a second phase which separated when cooled.

Analysis.—Two small portions of the product solution were titrated[5] for hydroperoxide. Based on the titration results, a 10–20% excess of triphenylphosphine was added to the reaction mixture and allowed to stand for at least 1 hr to ensure complete reduction of the hydroperoxides.

Direct glpc analysis of the reduced solution did not give well-resolved separations; so the products were concentrated by removing most of the unreacted TMH *in vacuo* (5 mm at 40°). The pot residue was transferred quantitatively to a sample vial with a small amount of acetone; a known amount of dimethyl succinate or eicosane was added as an internal standard, and the solution was analyzed by glpc (5% nitrile–silicone XE-60 on Chromosorb Z, 6 ft × 0.125 in., temperature 60–200°, Aerograph 600 D). The glpc investigation of the distillate indicated that no significant amount of products was carried over. The response of the chromatograph to the 2,4,6-trimethyl-2,4-heptanediol and 2,4,6-trimethyl-2,4,6-heptanetriol relative to

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[16] A. D. Petrov, V. I. Sushchinskii, and L. D. Konoval-chikov, *Zh. Obshch. Khim.*, **25**, 1566 (1955); *Chem. Abstr.*, **53**, 4474*g* (1956).

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the internal standard, was determined and the appropriate correction factor was applied. This correction factor (same for both polyols) was assumed to be applicable to the unidentified peaks in the glpc trace. The 2,4- and 2,6-diols eluted simultaneously by the chromatographic technique used in this study.

Registry No.—**3,** 2613-61-8; 2,4,6-trimethyl-2,4-heptanediol, 33070-42-7; 2,4,6-trimethyl-2,6-heptanediol, 33070-43-8; 2,4,6-trimethyl-2,4,6-heptanetriol, 33070-44-9.

Lithium–Ammonia Reduction of Benzaldehydes to Toluenes

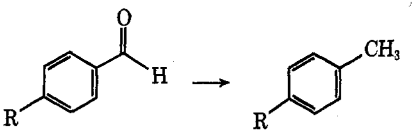
STAN S. HALL,* ANNE P. BARTELS, AND ARLENE M. ENGMAN[1]

Department of Chemistry, Rutgers University, Newark, New Jersey 07102

Received August 16, 1971

Two methods are reported for the reduction of benzaldehydes to toluenes in lithium–ammonia solutions. By these methods *p-tert*-butylbenzaldehyde, *p*-isopropylbenzaldehyde, *p*-methylbenzaldehyde, and benzaldehyde were reduced to *p-tert*-butyltoluene, *p*-cymene, *p*-xylene, and toluene, respectively. Both methods take advantage of good proton sources to minimize a serious competitive reaction which leads to dimers. Mechanistic implications are discussed.

The only reported reduction of an aldehyde in metal–ammonia solutions is that of vanillin to vanillyl alcohol plus a dimer in potassium–ammonia.[2] Presumably the reduction of aldehydes in liquid ammonia has been avoided because aldehydes readily condense with ammonia.[3] We have found that aromatic aldehydes are amenable to metal–ammonia conditions and wish to describe two useful methods for their reduction to toluenes.



R = *tert*-C_4H_9, *iso*-C_3H_7, CH_3, H

Recently we reported conditions for the reduction of aromatic ketones to aromatic hydrocarbons in lithium–ammonia (THF) solutions.[4] Extensions of this work to aromatic aldehydes[5] led to the following observations: (1) the aromatic aldehydes were reduced substantially faster than aromatic ketones; (2) trace amounts of cobalt had no noticeable reduction rate enhancement effect as was observed with aromatic ketones; and (3) aromatic aldehydes dimerize much more readily than aromatic ketones.[6]

The formation of dimers made the method inutile for our purposes as a synthetic reaction and consequently a modified method was sought which would minimize their formation. Since dimers had not been observed in the reduction of benzyl alcohols when subjected to these conditions,[7] thus excluding the possibility of dimer formation from the benzyl radical **5**, we assumed the ketyl radical **2a** to be the source of dimers.[8,9] It was reasoned that if the ketyl radical **2b** would be formed in the presence of a good proton source, such as *tert*-butyl alcohol or ammonium chloride, it might be quickly protonated forming the alkoxy radical **3**, which in turn would be rapidly reduced to the benzyl alkoxide **4**. The net effect should be a substantial decrease in the amount of dimer formed. Following this presupposition, two useful methods were developed and are described. The product toluene normally represented more than 90% of the chromatographable material and was usually isolated pure in at least 80% yield using either method.

Method A involves the addition of a solution of the benzaldehyde and *tert*-butyl alcohol in THF to a refluxing lithium–ammonia solution, followed by an ammonium chloride quench. Substituting sodium benzoate[10] for the ammonium chloride yielded mainly the toluene along with lesser amounts of the benzyl alcohol and aldehyde (*ca.* 5:1.5:1) indicating that the ammonium chloride quench is necessary to complete the reduction.

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[3] (a) R. L. Augustine, Ed., "Reduction," Marcel Dekker, New York, N. Y., 1968, p 116; (b) H. Smith, "Organic Reactions in Liquid Ammonia. Chemistry in Nonaqueous Ionizing Solvents," Vol. I, Part 2, Wiley, New York, N. Y., 1963, pp 123 and 216.

[4] S. S. Hall, S. D. Lipsky, F. J. McEnroe, and A. P. Bartels, *J. Org. Chem.*, **36**, 2588 (1971).

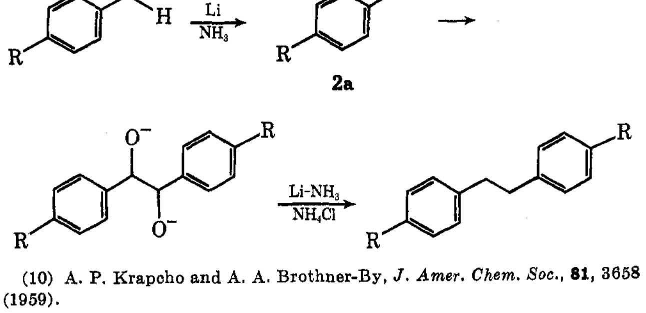
[5] The benzaldehyde in THF was added slowly (*ca.* 20 min) to a lithium–ammonia (THF) solution. After 20 min at reflux the mixture was cautiously quenched with excess ammonium chloride.

[6] The following interesting toluene/aromatic hydrocarbon dimer (2) ratio was observed for *p-tert*-butylbenzaldehyde, *p*-isopropylbenzaldehyde, *p*-methylbenzaldehyde, and benzaldehyde, respectively: 82/18, 77/23, 60/40, and 56/44. After analysis by glc the monomer–dimer aromatic hydrocarbon mixture was eluted from an alumina column with petroleum ether (bp 38–58°) and then distilled apart at reduced pressures. Spectral data (ir, nmr, and mass spectra) indicated the major dimer to be a 1,2-diarylethane. Perhaps the most revealing were the mass spectra. For example, 1,2-*p,p'*-dicumylethane from *p*-isopropylbenzaldehyde, *m/e* (rel intensity) 133 (100), 266 (8, M^+). In addition, the major dimer from the reduction of benzaldehyde was compared with an authentic sample of 1,2-diphenylethane.

[7] (a) S. S. Hall, S. D. Lipsky, and G. H. Small, *Tetrahedron Lett.*, 1853 (1971); (b) G. H. Small, unpublished results.

[8] (a) W. E. Bachmann, *J. Amer. Chem. Soc.*, **55**, 1179 (1933); (b) C. B. Wooster, *ibid.*, **59**, 377 (1937).

[9] We assumed the major dimer to be formed according to the following general scheme *via* a bimolecular reduction.



[10] A. P. Krapcho and A. A. Brothner-By, *J. Amer. Chem. Soc.*, **81**, 3658 (1959).