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Relative Reactivities in Oxidations of Polypropylene and Polypropylene Models

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ABSTRACT: The oxidations of solid polypropylene in bulk and solution and of its liquid models, 2,4-dimethylpentane and 2,4,6-trimethylheptane, give ratios of rate constants for propagation and termination, $k_p/(2k_t)^{1/2}$, at several temperatures that fall clearly into three groups. This ratio is highest for bulk atactic polypropylene where propagation is limited to radicals that escape from the cage and can be scavenged, intermediate for polymer in both bulk and solution if all the initiating radicals are considered, and smallest for the models. Differences are due mostly to changes in termination constants but also to steric effects on inter- and intramolecular propagation. Difficulties in radical separation and combination are compensating. Sequence lengths in oxidations of polypropylene are discussed.

In 1973, Niki, Decker, and Mayo[1] reported rates and rate constants for oxidations of bulk atactic polypropylene (APP) and compared them with the corresponding relations for the model, 2,4-dimethylpentane (DMP)[2], at 45 to 55 °C. This comparison requires an appreciation of the very low efficiency of chain initiation in unplasticized bulk APP (formation and separation of two $PPO_2\cdot$ radicals) and the related very low termination constant for the combination of two free $PPO_2\cdot$ radicals. The low efficiency of initiation arises from both the low efficiency of utilizing initiator radicals to make $PP\cdot$ radicals and the low probability ($\sim$16% at 45 °C)[3] that the resulting $PPO_2\cdot$ radicals will separate and propagate before they terminate. The comparison also requires an appreciation of the importance of sequence lengths. In the oxidation of bulk DMP at 50 °C, intramolecular propagation is so much faster than intermolecular propagation that 83% of the DMP reacting gives dihydroperoxide.[2] Similarly, 2,4,6-trimethylheptane (TMH) appears to give a high proportion of trihydroperoxide, but only at <1% conversion.[4] In APP, sequence lengths are not well known,[5] in spite of claims to the contrary,[6,7] and comparisons with models must be based on averages of unknown proportions of slower intermolecular and faster intramolecular propagations in APP.

A 1975 paper by Chien and Wang[8] presents new data on the oxidation of bulk APP and purports to show that the ratios $k_p/k_t^{1/2}$ (rate constants for propagation and termination) for bulk APP, isotactic polypropylene (IPP), and their models, DMP and TMH, all fall on the same Arrhenius plot. My present paper shows that this conclusion is the result of misunderstanding or misinterpretation of published data, which I admit are somewhat confusing. When an early draft of this manuscript was sent to known contributors to the field, their responses produced some additional data and corrections of old data. Incorporation of these, together with some corrections and additions to our previous work, now leads to a consistent

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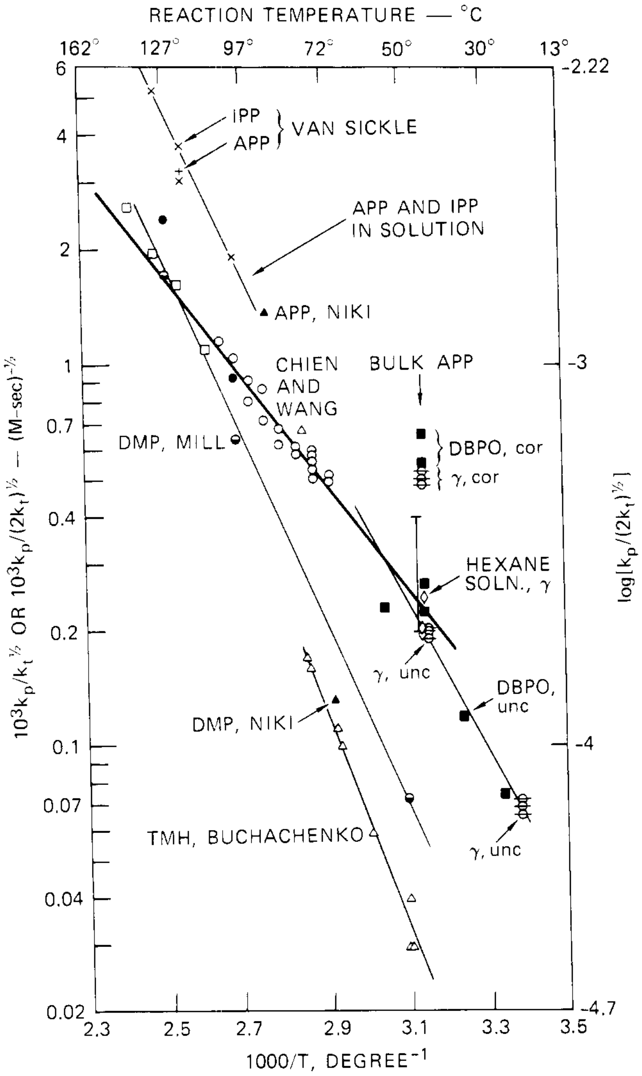

Figure 1. Rates of oxidation of APP, IPP, and models as a function of temperature; correction and expansion of Figure 8 of Chien and Wang.[1]

pattern for all data except those of Chien and Wang and extension to rate constants for oxidations of PP in solution. The problem of sequence lengths in oxidations of APP is also considered. My conclusions are summarized in the last section.

Ratios of Rate Constants and Temperature Coefficients

Figure 1 is a reproduction and expansion of Figure 8 of Chien and Wang,[8] showing $k_p/k_t^{1/2}$ as a function of reciprocal absolute temperature. (The k_t of Chien and Wang[8] and of Buchachenko et al.[9] correspond exactly to the $2k_t$ in the other references cited.) The original figure included the heavy line, the associated open circles (benzoyl peroxide catalyzed oxidations of bulk APP at 71–105 °C) and open squares (thermally-initiated oxidations of IPP at higher temperatures), the 100 and 125 °C solid circles of Mill and Montorsi on DMP,[2] one open triangle at 80 °C for the data of Buchachenko et al. on TMH at 6–78 °C,[9] and the vertical bar to represent the data of Niki, Decker, and Mayo[1] on oxidations initiated by di-*tert*-butylperoxy oxalate (DBPO) at 45 °C. The 50 °C point of Mill and Montorsi for DMP and the data of Buchachenko et al. on TMH at other temperatures were omitted. However, all the DMP and TMH points included by Chien and Wang are represented incorrectly. Their data on APP are based on concentrations of C_3H_6 units, i.e., tertiary hydrogen atoms, but the DMP points are too high by a factor of near $2^{1/2}$ and the TMH points correspond to molar concentrations. To be comparable with the APP data, the molar DMP rates must be divided by two and the molar TMH rates by three. The correct DMP points (semisolid circles) now lie on the next to lowest line. Professor Buchachenko has recalculated[10] his previous TMH data, correcting for oxygen consumed in initiation; these data are represented by the open triangles on the lowest line. Figure 1 also includes one point for DMP at 70 °C by Niki et al.[11] (solid triangle), which falls between the DMP and TMH lines. In the present figure, all the values of $k_p/(2k_t)^{1/2}$ or $k_p/k_t^{1/2}$ are based on total oxygen absorption per tertiary hydrogen atom, which includes both inter- and intramolecular propagation. The oxygen absorptions are for propagation only except for the Mill and Montorsi data[2] and some data with PPs[12] where small contributions from initiation and termination are included.

I now take up the representation of our own data on APP[1,13] at 45 °C. Chien and Wang have omitted reference to our best data, that on γ-initiated oxidations of APP by Decker and Mayo.[3] New points (⊖ = γ_{unc}) at three different dose rates are shown in Figure 1 at the bottom of the vertical bar of Chien and Wang, but they require adjustment. The Chien and Wang data on APP are based on rates of initiation of chain oxidations by free radicals that have escaped interaction of the original pair and can be scavenged by inhibitors. The uncorrected γ data of Decker et al.[3] are based on all the APP peroxy radicals produced, whether or not they escaped cage interaction. Experiments with 2,6-di-*tert*-butyl-*p*-cresol[3] showed that at 45 °C this reagent could scavenge only the 16% of the radicals that escaped the cage and could propagate chains; the other 84% reacted with each other before any propagation occurred. When the lower γ_{unc} values of $k_p/(2k_t)^{1/2}$ in Figure 1 are corrected to count only radicals capable of propagation (as in the Chien and Wang experiments), then the values are 2.5 times as large (γ_{cor}) and lie well above the bar in Figure 1.

The DBPO data of Niki et al.[1] present other problems. First, some errors have been found and noted along with the reference.[1] DBPO apparently acts as a plasticizer in APP (Tables II and III in ref 1); as the concentration of DBPO increases, the efficiency of production of APP peroxy radicals increases, but the values of $k_p/(2k_t)^{1/2}$ decrease because termination becomes faster. Therefore, the value of the ratio for the lowest concentration of DBPO should be nearest to the value in unplasticized APP, and this value is shown as the lowest solid square at 45 °C. The extrapolated value of the ratio[14] at zero initiator concentration is 2.7×10^{-4} and is represented by the next lowest solid square at 45 °C in Figure 1.

The efficiency of initiation as given by Niki et al.[1] refers to the ability of the *tert*-butoxy radicals from decomposing DBPO to produce APP peroxy radicals, regardless of whether the latter escape the cage. We do not know the efficiency of cage escape for the APP peroxy radicals in APP in the presence of plasticizing DBPO, but we expect it to be higher than in the γ-initiated oxidations with no DBPO and thus to require less correction. The two highest solid squares at 45 °C, corresponding to the 16% cage escape of APP peroxy radicals observed with γ radiation and no DBPO, probably represent some over-correction for the two lower squares, and thus are consistent with the γ_{cor} values, which are the best available.

The points and highest lines in Figure 1 are for oxidations of PP in solution. The + and x's and light line are calculated from the data of Van Sickle[12] for APP and IPP, respectively, in benzene at 100 to 135 °C, mostly at 1.5 to 1.6 M; the solid triangle is the datum of Niki and Kamiya[15] for 1 M APP in chlorobenzene at 90 °C. As pointed out by Van Sickle,[12] IPP oxidizes a little faster than APP, but the agreement between the Van Sickle and Niki data is remarkably good.

Most of the remainder of this section shows how increasing ease of separation of $2PPO_2\cdot$ radicals from the initial cage where they cannot be scavenged to a state where they can is closely compensated by an increased ease of radical combination. The simplest example in Figure 1 is the near identity of the hexane and uncorrected γ bulk points at 45 °C, both based on known rates of production of pairs of $PPO_2\cdot$ radicals. If we apply a correction to count only the 16% of radicals that escape the cage in bulk, then $k_p/(2k_t)^{1/2}$ becomes larger by a factor of 2.5, because the calculated k_t is smaller. (In Figure 1, the calculation $k_p/(2k_t)^{1/2}$ in hexane assumes that all the initial $PPO_2\cdot$ radicals can separate. If, for example, only 80% of them actually separate, then k_t must be decreased by 10%, and so on.)

Decker[3] used γ radiation to initiate oxidations of a wide range of hexane–APP mixtures at 45 °C. At either 650 or 1750 rad/min, the cooxidation is an ideal one and the rate is a linear function of the concentration of APP (expressed in g/100 mL) from pure hexane to bulk APP, for which the rates differ by a factor of 20 or more. This linear relation shows that there are no abnormalities in interactions of different peroxy radicals;[16,17] it means that as bulk APP is diluted with hexane at constant dose rate, $(R_i/2k_t)^{1/2}k_p$ for APP does not change perceptibly and implies (for an oxidation that is first order in APP) that the major changes in efficiencies of initiation (R_i) found by Niki[1] with pentane and DBPO are also closely compensated by changes in k_t.[18]

On this basis, hexane points below 45 °C, if they were available, would also coincide with the uncorrected γ bulk points at these temperatures and the line through these points at 22 to 45 °C coincides, well within experimental error, with the line for solutions above 95 °C. However, there must be considerable coincidence in this agreement; Van Sickle[12] found that his oxidations of APP and IPP are 0.73 order in substrate and so the calculated values of $k_p/(2k_t)^{1/2}$ will depend on the concentration of PP. (The lowest 120 °C point is for 4.0 instead of 1.5 M IPP.) This low order is attributed to a low dependence of intramolecular propagation on PP concentration.

In Figure 1, the line for all the points for PP in solution is nearly parallel with the lines for DMP and TMH. The differences in ordinates at 45 °C correspond to ratios of 3.5 and 8, respectively, and to 3.0 for DMP at 100 °C. The section on Absolute Rate Constants concludes that differences are due mostly to long sequences of peroxide groups in the polymer. There is an additional factor of 2.5 in $k_p/(2k_t)^{1/2}$ at 45 °C between data on corrected bulk and solution APP due to viscosity effects.

Sequence Lengths in Oxidations of APP

The conclusions of Chien and co-workers about sequence lengths in the oxidation of PP at 100 °C have been questioned previously;[5] those arguments need no repetition here. There are two different problems in sequence lengths, one at 50 °C and below where the PP polyperoxides are stable and another at 100 °C and above where they usually are not. I expand here a recent suggestion by T. Mill. In the oxidation of neat DMP at 50 °C, the ratio of di- to monohydroperoxide is[2]

$$D/M = k_r/13k_p' = 4.9$$

where k_r and k_p' are the rate constants for intramolecular and intermolecular propagation and the molar concentration of tertiary hydrogen atoms in neat DMP is 13; k_r/k_p' is then 63. In the neat APP at 50 °C, the molar concentration of tertiary hydrogen atoms is about 20 M; and if k_r/k_p' is the same as in DMP (but see below), D/M in APP is then only 3.15 (because of the higher concentration of tertiary hydrogen atoms in APP). On this basis, for long kinetic chains, most of the $PPO_2\cdot$ radicals would have a 24% chance of reacting intermolecularly. However, because the first $PPO_2\cdot$ radical in each sequence can react intramolecularly in two directions, only 14% of these radicals should react intermolecularly. Thus, 14% of the peroxide sequences will contain single units, 20% two units, 16% three units, 12% four units, and 38% will contain five or more units. Although 14% of the *sequences* will contain isolated PPO_2H groups, the other sequences will average about five units and so the proportion of *all* the hydroperoxide groups that is isolated will be only about 3%. Thus, the quantitative determination of isolated groups will be difficult even if they comprise 14% of the sequences.

At 50 °C or below, the proportions of oxidation products at constant rate of initiation are independent of reaction time and conversion and 50 to 100 hydroperoxide groups are formed per $PPO_2\cdot$ radical that escapes from the initiating cage.[3] Thus, fairly long sequences of fairly stable hydroperoxides are expected.

At 100 °C, the concentration of tertiary hydrogen atoms in DMP is 12 M: D/M is 6.9, and k_r/k_p' is 83. By the method used above, D/M for 19 M tertiary hydrogen in APP is 4.36; for long kinetic chains, 10% of the sequences would contain one hydroperoxide unit, 17% two units, 14% three units, 11% four units, and 48% five or more units. However, although hydroperoxides are the major primary oxidation product at 100 °C, they are unstable. From oxidations of PP in benzene solutions at 100 °C, Van Sickle concluded that most of the oxygen absorbed, at conversions above 1–2%, appeared in groups other than hydroperoxide groups. Thus, the average number of hydroperoxide groups in 1,3 sequences at 100 °C decreases rapidly to <2 above 1% conversion.

The calculations above assume that k_r/k_p' is the same for DMP and APP at the same temperature. However, Niki and Kamiya[15,19] have shown that APP is less susceptible to external attack by free radicals than would be expected from results with 2,4-dimethylpentane. These results will be considered further in the next section, but the effective values of k_r/k_p' in APP and the tendency to form long sequences may be significantly larger than those calculated just above.

Absolute Rate Constants

Table X in one of our previous papers[1] compared k_p and k_t in oxidations on DMP and APP at 45 °C. Since then, a typographical error and an error of a factor of 2 in our APP calculations have been discovered.[1] Table I is a revision and extension of our earlier Table X. It corrects the errors, puts the DMP (like the APP) data on the same per hydrogen basis, compares values of $(2k_t)^{1/2}$ instead of k_t (which exaggerates experimental errors), and incorporates some additional data.

The most reliable values in Table I are those for $k_p/(2k_t)^{1/2}$; they come directly from simple measurements of rates of oxidation. The principal difficulty arises from the composite nature of k_t when most of the oxidation takes place at tertiary hydrogen atoms. Termination constants for tertiary peroxy radicals are very small, but these terminations are inevitably accompanied by nontermi-

Table I

Rate Constants in M/s for Oxidations at 45 °C[a]

	2,4-dimethylpentane		polypropylene			
			hexane soln,[3] APP	bulk APP, mol/kg/s[13]		
rate constants or ratios	Howard[21]	Mill[2]		uncorr[1]	corr[b]	Chien,[8] APP[c]
$k_p \times 10^2$	0.50 (15.4)[21]	1.8[d] (14.1) 1.0 + 0.8[e]	39[f] 98[g]	0.38 (15)	0.38	8.3 (12.1)
$(2k_t)^{1/2}$ (or $k_t^{1/2}$)	161[f]	320[d] (6.8)	1700[22]	17 (13)	6.8	350 (11.6)
$k_p/(2k_t)^{1/2} \times 10^4$	0.31	0.56[h] (10.7)	2.3 14.8[g]	2.3[i] (10.5)[j]	5.5	2.3 (6.3)

[a] For rates of oxygen absorption in propagation, intermolecular and intramolecular (except as noted), per tertiary hydrogen atom. Activation energies are in parentheses and apply to k_t (not $k_t^{1/2}$). [b] On assumption that $^1/_6$ of the $PPO_2\cdot$ radicals produced in the initiating cage escape and propagate at 45 °C. [c] Extrapolated from 70 °C and above. [d] Extrapolated from 100 °C. [e] Contributions of intermolecular (first) and intramolecular attack for average sequence length of 1.83 in DMP. [f] Calculated from other constants in the same column. [g] Values for APP in chlorobenzene at 90 °C, for k_p with and for $k_p/(2k_t)^{1/2}$ without 1.6 M t-BuO_2H.[15] [h] Extrapolated from 50 °C. [i] Value for lowest DBPO in Table II in ref 1. [j] E for $k_p/(2k_t)^{1/2}$ is from ref 3 and the 25 and 45 °C runs in ref 1, and should be equal to $E_p - E_t/2$. Apparently the listed E_p is too low or the listed E_t is too high, or both.

nating interactions of tertiary peroxy radicals that produce alkoxy radicals,[20] and then by their cleavage, primary and secondary peroxy radicals with high termination constants. Thus, small proportions of cleavage can drastically increase the average termination constant. The average termination constants can be meaningful under carefully specified conditions, but values extrapolated from other temperatures are suspect because the proportions of tertiary, secondary, and primary peroxy radicals change.

Of the propagation constants in Table I, I think that Howard's value[21] for k_p for t-$BuO_2\cdot$ + DMP, 0.0050 for intermolecular attack only, is probably the best value. The corresponding value of Mill and Montorsi,[2] for DMP peroxy on DMP, extrapolated from 100 °C, is the same within experimental error. The effective $k_p/(2k_t)^{1/2}$ in the Howard column is the $^5/_9$ of the Mill value that is attributed to intermolecular propagation. The $(2k_t)^{1/2}$ value in the Howard column is calculated from the numbers above and below it. The $(2k_t)^{1/2}$ for the hexane solution of APP is the square root of the value of k_t for secondary heptylperoxy radicals.[22]

It is now clear that differences in k_p and $k_p/(2k_t)^{1/2}$ for DMP and APP in bulk and solution cannot be accounted for solely by viscosity effects on chain termination, as we tried to do in our previous paper,[1] and that special steric effects in propagation in 2,4-dimethylalkanes must also be considered. Brook[23] showed that 2,3-dimethylbutane and 2,5-dimethylhexane are nearly twice as reactive as DMP toward *tert*-butoxy radicals at 135 °C. In intermolecular propagation with *tert*-butoxy radicals at 45 °C, Niki and Kamiya[19] found that DMP is only 59% as reactive as 2,3-dimethylbutane and 47% as reactive as calculated for an unhindered hydrocarbon; APP was still more hindered and had only 14% of the calculated reactivity. Mill and Montorsi[2] found that isobutane is 2.6 times as reactive as DMP at 100 °C on a per tertiary hydrogen basis in intermolecular propagation with peroxy radicals. Similar effects in polystyrene are much larger.[15,19] However, in oxidations in chlorobenzene solutions at 90 °C with 1.6 M *tert*-butyl hydroperoxide, which reduces but does not eliminate intramolecular propagation,[21] Niki and Kamiya[15] found that APP was twice as reactive as calculated for an unhindered hydrocarbon. Thus, the spiral conformation of APP permits a faster intramolecular propagation to more than compensate for the difficult intermolecular propagation in APP. The intermolecular propagation constants are in the order, per tertiary hydrogen, isobutane > DMP > APP.

On this basis, the larger k_p and $k_p/(2k_t)^{1/2}$ for APP in hexane at 45 °C, in comparison with those in DMP, are due mostly to extensive intramolecular propagation; this effect more than overcomes a $(2k_t)^{1/2}$ that is 5 to 10 times as great in hexane solution (from *sec*-hexyl-$O_2\cdot$ radicals) as in DMP. In bulk APP, I would expect the sequence lengths to be long, as in solution, but Table I shows that both k_p and $(2k_t)^{1/2}$ are only about one-hundredth as large in bulk as in solution. The k_t in bulk must be small to parallel the difficult separation of radical pairs in bulk APP.[1] The net effect of phase change from solution to solid on $k_p/(2k_t)^{1/2}$ is zero or an increase by a factor of $6^{1/2}$, depending on whether a correction is made for escape of only $^1/_6$ of the $PPO_2\cdot$ radicals from the initiating cage (Figure 1). The k_p's at 45 °C correspond to 0.076 propagation per peroxy radical per second in 20 M bulk APP, 0.39 in 1 M APP in solution, and 0.23 in neat DMP.

Although the value of $k_t^{1/2}$ for bulk PP in Table I is very small, it is consistent with some other termination constants in viscous media. Thus the square root of the apparent second-order k_t in M/s for the polymerization of methyl methacrylate at 22.5 °C decreases from 6650 at 0% conversion to 28 at 80% conversion and the radicals "terminate" by local exhaustion of monomer.[25] In the γ-initiated polymerization of ethylene at 30 °C and 400 kg/cm^2, the rate increases steadily with time as if immobilized, nonterminating, but propagating radicals were being produced in the polymer formed,[26] but this effect disappears between 86 and 100 °C.

Activation energies for chain propagation are similar for bulk APP and models, but activation energies for chain termination are about twice as large in bulk APP as for models.

Figure 1 shows that the values of $k_p/k_t^{1/2}$ of Chien and co-workers for IPP are consistent with those of the liquid models, DMP and TMH, near 125 °C and, after extrapolation, their data for APP are consistent with ours for APP in solution at 45 °C. Their termination and propagation constants approach those of a liquid or solution. Their low values of $k_p/k_t^{1/2}$ at high temperatures might be due to high conversions and accompanying low viscosity and higher k_t,[5] and/or to a diffusion-limited rate.[24] Their difficulties became less serious at lower rates and temperatures.

Conclusions

Literature data on oxidations of APP in bulk, APP and IPP in solution, and liquid models, 2,4-dimethylpentane and 2,4,6-trimethylheptane, have been organized and presented on a consistent basis, the total rate of O_2 consumption per tertiary hydrogen atom in the substrate, expressed as $k_p/(2k_t)^{1/2}$, where k_p is the average of the k_p

for the first attack on the substrate by a peroxy radical (intermolecular propagation) and all the subsequent intramolecular propagations, the average sequence lengths in the latter probably being ≥5. The much higher average rate of propagation in APP in solution than for DMP is due to the high preference for intramolecular oxidation in APP,[15,19] which is also sufficient to compensate for a higher rate constant for chain termination in APP in hexane solution. However, in bulk APP, both propagation and termination are much slower than in solution. The compensation is such that $k_p/(2k_t)^{1/2}$ for bulk and solution APP are the same for the same rate of formation of initiating $PPO_2\cdot$ radicals, but that the ratio for bulk APP is greater on the basis of free scavengeable radicals. Thus, the $k_p/(2k_t)^{1/2}$ for oxidations of solution and bulk APP are the same at the same rate of decomposition of initiator. These relations appear to be consistent over a wide temperature range; agreements on rates for the models and for APP in solution are good to remarkably good, considering that results were obtained in different laboratories.

This paper and a previous one[5] have emphasized problems that I have found with the published work of Chien and co-workers on oxidations of PP. However, they have made many useful contributions to the field, and we agree on more points than we disagree. Their last paper stimulated preparation of this one, in which other workers in the field have been able to examine the use of their data, and from which some new and clear patterns emerge.

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References and Notes

(1) E. Niki, C. Decker, and F. R. Mayo, *J. Polym. Sci., Polym. Chem. Ed.*, 11, 2813 (1973); correction, *ibid.*, **13**, 2415 (1975). Further, in the last line of Tables II and IV, all the values of $k_p/(2k_t)^{1/2} \times 10^4$ should be divided by 2.00. As a result, all the values of k_p and $k_p/(2k_t)^{1/2}$ for APP in Table X should also be divided by 2.00. These results are in mol/kg; cf. Note 13. For DMP in Table X, $k_p/(2k_t)^{1/2}$ should read 0.000026 instead of 0.00027.
(2) T. Mill and G. Montorsi, *Int. J. Chem. Kinet.*, **5**, 119 (1973). In the last line in Tables I and II, $k_p/(2k_t)^{1/2}$ corresponds to total O_2 absorbed per tertiary hydrogen, per molecule per min; "$\times 10^3$" should be inserted after $k_p/(2k_t)^{1/2}$ in Tables II and VI; these ratios are divided by $60^{1/2}$ to convert minutes to seconds in the present paper. The $k_p/(2k_t)^{1/2} = 3.2 \times 10^{-4}$ (M s)$^{-1/2}$ at 100 °C near the bottom of p 130 is for intermolecular reaction only per tertiary hydrogen; when intramolecular reaction is included, as in my Figure 1, the ratio is nearly twice as large. Small changes in ratios of rate constants should be made on p 134: $k_r = 83 \times 0.23 = 19.1$ s^{-1}; $k_r/k_p' = 83$. The 0.23 value for k_p at 100 °C is the rate of disappearance of DMP per tertiary hydrogen in cooxidation with isobutane, i.e., the rate of incorporation of the first oxygen molecule. However, each of these reactions is associated with an average uptake of 0.87 molecules of additional oxygen by intramolecular reaction so that the overall value of k_p is $1.87 \times 0.23 = 0.43$.
(3) C. Decker and F. R. Mayo, *J. Polym. Sci., Polym. Chem. Ed.*, **11**, 2847 (1973); correction, *ibid.*, **13**, 2415 (1975). In Table XII of this paper, delete "%" in "Efficiency, %." For the first four experiments for PP in hexane in Table XI, values of $k_p/(2k_t)^{1/2}$ in (M s)$^{1/2} \times 10^3$ have recently been calculated as 0.25, 0.25, 0.20, and 0.216, assuming 100% escape of $PPO_2\cdot$ radicals from the hexane cage, and plotted in Figure 1 in the present paper.
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(11) E. Niki, Y. Takaishi, and Y. Kamiya, *Nippon Kagaku Kaishi*, 1559 (1975). Their $k_p/(2k_t)^{1/2}$ at 70 °C is 7.0×10^{-5} (M s)$^{-1/2}$ for intermolecular propagation only per tertiary hydrogen atom, 13.3×10^{-5} for combined intermolecular and intramolecular propagation.
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(13) In ref 1 and 3, rates and concentrations are expressed in mol/kg, but other data in Figure 1 are in mol/L. The density of APP is 0.85 at 25 °C (J. Brandrup and E. H. Immergut, "Polymer Handbook", 2nd ed, Interscience, New York, N.Y., 1975). In the relation, $-d[O_2]_p/dt = (R_i/2k_t)^{1/2}k_p[PP]$, a similar change in concentration units on both sides of the equation has no effect on $(R_i/2k_t)^{1/2}k_p$ but if R_i decreases by a factor, x, $k_p/(2k_t)^{1/2}$ increases by $x^{-1/2}$, and vice versa. Hence, the mol/kg values for bulk APP in Figure 1 and Table I should be multiplied by 1.09 to be exactly comparable to the other mol/L data.
(14) When the ratios $k_p/(2k_t)^{1/2}$ for experiments 28, 31, and 29 at 45 °C in Table II of ref 1 are plotted against the initial concentrations of DBPO, they fall nearly on a straight line.
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(18) $G_{R\cdot}$ in hexane at 45 °C is 7.8, in bulk APP, 11.0;[3] further, as shown in the next paragraph, oxidations of PP are only 0.73 order in this substrate. However, the resulting differences in R_i and $R_i^{1/2}$ and effects on k_p are not important to the argument.
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(21) J. A. Howard, private communication. k_p is for intermolecular propagation only by t-$BuO_2\cdot$ + DMP in the presence of 0.4 M t-BuO_2H (which reduces but does not exclude intramolecular propagation). The overall value of k_p at 30 °C, 0.0026 per tertiary hydrogen, includes 0.0015 for intermolecular propagation and 0.0011 for intramolecular propagation. E_p for t-$BuO_2\cdot$ and isooctane is 15.4 kcal/mol; use of this value for DMP gives the $k_p = 0.0050$ at 45 °C in Table I.
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(24) The films of Chien and Wang[8] were much thicker (100 μm instead of less than 1 μm in our dispersions on quartz wool)[1,3] and their rates of oxidation (oxygen demands) were much higher (5 to 260×10^{-6} M/s instead of 1.4 to 3×10^{-6} M/s) than in our γ-initiated experiments.
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