Electron Spin Resonance of Transient Radicals during Pyrolysis and Photolysis. Benzyl Ether

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Benzyl ether has been pyrolyzed at 452, 474, and 497 °C at a pressure of 20.7 MPa. Benzyl has been observed by ESR, and product analyses have been made. The reaction $C_6H_5\dot{C}HOCH_2C_6H_5 \rightarrow C_6H_5CHO + C_6H_6\dot{C}H_2$ is part of a proposed scheme. This reaction was separately studied photolytically by preparing the reactant radical with benzyl ether and an initiator in benzene solution. Measurements from 105 to 155 °C at 6.9 MPa gave an activation energy of 15.5 kcal/mol (±15%) and an estimate of the Arrhenius A factor of 1 × 10¹² s⁻¹. The varous results are discussed in terms of a free-radical chain reaction. Methylcyclohexadienyl was also prepared, and ESR parameters are given.

Recent studies^{1,2} have been made on the pyrolysis of benzyl ether. These studies were concerned with processes taking place in the conversion of coal to fluid products and benzyl ether was chosen as a model compound for some of the oxygen bound in coal as ethers. Schlosberg and co-workers¹ have pyrolyzed benzyl ether at 450 °C in a tubing bomb. Toluene and benzaldehyde were major products. Substantial amounts of other products were also found which were regarded largely as secondary products arising from decomposition of benzaldehyde at 450 °C. A scheme proposed to account for the large yields of toluene and benzaldehvde was based on a free-radical chain process. A concerted process was also considered. Gilbert and Gajewski² carried out kinetic experiments by pyrolyzing gas-phase and liquid-phase benzyl ether contained in sealed ampules. Temperature from 310 to 350 °C were used, and assays were made of the rate at which benzyl ether was converted to products. The reaction order and activation energy were regarded as consistent with freeradical chain processes, and no evidence for concerted reactions was found. Equal amounts of toluene and benzaldehyde were formed from the pyrolyses. A scheme presented to account for the results is

$$C_6H_5CH_2OCH_2C_6H_5 \rightarrow C_6H_5CH_2O + C_6H_5CH_2 \quad (1)$$

$$C_{6}H_{5}CH_{2}\dot{O} + C_{6}H_{5}CH_{2}OCH_{2}C_{6}H_{5} \rightarrow C_{6}H_{5}CH_{2}OH + C_{6}H_{5}\dot{C}HOCH_{2}C_{6}H_{5}$$
(2)

$$C_{6}H_{5}CH_{2} + C_{6}H_{5}CH_{2}OCH_{2}C_{6}H_{5} \rightarrow C_{6}H_{5}CH_{3} + C_{6}H_{5}\dot{C}HOCH_{2}C_{6}H_{5}$$
(3)

$$C_6H_5\dot{C}HOCH_2C_6H_5 \rightarrow C_6H_5CHO + C_6H_5\dot{C}H_2$$
 (4)
1

$$2C_6H_5\dot{C}H_2 \rightarrow C_6H_5CH_2CH_2C_6H_5$$
(5)

Thermal initiation is through eq 1 while eq 2 is a transfer reaction in which $C_6H_5CH_2O$ is converted to 1. Equations 3 and 4 constitute the chain while eq 5 is a typical termination process. The free-radical chain process considered by Schlosberg and co-workers¹ was identical except that they did not consider the fate of $C_6H_5CH_2O$ which is given by eq 2.

We have developed³ an ESR method for obtaining well-resolved spectra at high temperatures and high pressures. In favorable cases the spectra of short-lived free radicals at steady-state concentration can be obtained during pyrolysis. We initiated a study of benzyl ether because of its interest as a model compound in coal conversion processes but now have added interest because of the above recent studies. We have arrived at the same reaction scheme presented above. In this paper we present our ESR observations during pyrolysis of benzyl ether. Product analyses have also been made and are presented. A newly added experimental capability is photolysis at high temperatures and pressures, and a major part of this paper is the singling out of eq 4 for detailed ESR study where 1 was prepared photolytically with an initiator.

Experimental Section

The ESR spectrometer operated at 9.2 GHz and utilized 100-kHz magnetic field modulation. The method of studying fluids at high temperatures and pressures has been described⁴ in detail. A liquid sample is pressurized and allowed to flow through a fused silica capillary that traverses the microwave cavity of the ESR spectrometer. The capillary is heated with hot air, and as the liquid arrives at the cavity the temperature increases rapidly, achieves a plateau through the active region of the cavity, and then falls rapidly upon exiting the cavity. All liquid samples were purged with helium in order to remove dissolved oxygen, and a pumping rate of 1.0 cm³/min was used. Samples were not recirculated through the hot zone. In pyrolytic experiments samples of the exiting liquid were collected for GC analyses during the recording of the ESR spectra. Normally temperatures are measured with a thermocouple located outside the capillary in the stream of hot air, and a calibration procedure⁴ is used in which a very small diameter thermocouple is threaded into the capillary. During pyrolytic experiments this outside thermocouple was used, and the accuracy of temperatures deduced for the interior of the capillary is estimated to be ± 2 °C. During photolytic work the calibration thermocouple was allowed to remain in the interior of the capillary, and the estimated accuracy is ± 1 °C. An assay was made of free-radical concentration during pyrolysis. A newly developed method⁵ involving spectral simulations was utilized which is well suited to weak spectra consisting of closely spaced hyperfine components. The estimated accuracy is $\pm 30\%$.

A few photolytic experiments were done near room temperature and at atmospheric pressure with an exper-

⁽¹⁾ Schlosberg, R. H.; Ashe, T. R.; Pancirov, R. J.; Donaldson, M. Fuel 1981, 60, 155-7.

⁽²⁾ Gilbert, K. E.; Gajewski, J. J., submitted for publication.
(3) Livingston, R.; Zeldes, H.; Conradi, M. S. J. Am. Chem. Soc. 1979, 101, 4312-9.

⁽⁴⁾ Livingston, R.; Zeldes H. Rev. Sci. Instrum. 1981, 52, 1352-7.
(5) Zeldes, H.; Livingston, R. J. Magn. Reson. 1982, 49, 84-92.



Figure 1. The spectrum of benzyl (top), 3.0×10^{-7} M, obtained during the pyrolysis of benzyl ether at 497 °C and 20.7 MPa. A spectral simulation is also shown.

imental configuration consisting of a flat fused silica cell within the microwave cavity through which the liquid sample was slowly flowed. Ultraviolet light from a 500-W high-pressure mercury arc (Philips Type SP500W) was brought to a focus upon the cell within the cavity by fused silica lenses. The need arose in this work for photolyses at high temperatures and high pressures, and the above described high-temperature equipment was provided with a similar UV lamp and lenses. Using the high-pressure capillary as a photolytic cell was less favorable than the customary flat cell used at atmospheric pressure, and a test at room temperature indicated approximately a factor of 2 loss in signal-to-noise ratio.

Pyrolytic work was carried out at a pressure of 20.7 MPa (200 atm) and photolytic work at elevated temperatures at 6.9 MPa.

GC analyses were carried out with a Hewlett Packard Model 5880A gas chromatograph provided with a 12-m methyl silicone (SP-2100) fused silica capillary column and a flame ionization detector. Identifications of peaks were made by comparing retention times with those from authetic compounds and were verified by GC MS. Weighed quantities of authentic compounds were used as quantitative standards.

Benzyl ether (Aldrich, 99%) was purified by vacuum distillation using a 76-cm column containing a spinning monel band and was stored under argon. Purified ether was used in all pyrolytic work. In photolytic work where large amounts of initiator were added both the as-received and purified ether were used. 2-, 3-, and 4-methyldiphenylmethane were synthesized from the corresponding methylbenzophenones by Clemmensen reduction. All other substances were readily available from commercial sources.

Results

Pyrolyses. The top part of Figure 1 shows the spectrum of benzyl obtained during the pyrolysis of benzyl ether at 497 °C. Below the experimental spectrum is a simulation using spectral parameters deduced for this radical in an earlier study³ where bibenzyl in toluene solution was examined at high temperature. No extraneous lines of other radicals are present, but because of the small signal-tonoise ratio lines from other radicals with strength up to 25% of those seen could have been missed. An assay gave 3.0×10^{-7} M for the concentration of benzyl. The spectrum becomes too weak at lower temperatures for assays of concentration. At 452 °C only the strongest lines can be discerned.

Quantitative GC analyses of major liquid constituents present after pyrolysis are given in Table I. Those components listed as others in Table I consist of a large number of substances no one of which is present in as large amount as that listed for benzene. Several substances verified as being present and also reported by Schlosberg and co-workers¹ are biphenyl, diphenylmethane, and 2- and 4-methyldiphenylmethane. There was concern that the

TABLE I: GC Analyses of Pyrolyzed Benzyl Ether

	wt % ^a		
component	452 °C	474 °C	497 °C
benzene	0.093	0.301	1.19
toluene	4.89	8.11	14.68
benzaldehyde	5.44	8.81	14.88
benzyl alcohol	0.012	0.052	0.225
bibenzyl	0.034	0.059	0.135
benzyl ether	89.30	82.17	67.53
others ^b	0.23	0.50	1.36

^a Normalized to 100%. ^b Proportion of total integrated GC area without calibration factors.

bibenzyl assay might be perturbed by 3-methyldiphenylmethane since the GC peaks of these substances fall at the same retention time. Cracking patterns from GC MS set a limit of 2.5% of the bibenzyl peak being 3-methyldiphenylmethane. A small amount of gas formed during pyrolysis. It was not assayed but has been reported¹ to be CO.

Photolyses. When the first pyrolytic experiment was carried out we anticipated eq 1-3 and expected that if any spectrum were observable it would be that of 1. Instead we saw 2 and with the aid of GC analyses adopted the scheme given by eq 1-5. It appeared that 1 was too short lived to be observable by ESR at pyrolytic temperatures.

A spectrum of 1 was obtained at room temperature and atmospheric pressure by photolyzing a 7% solution of di-*tert*-butyl peroxide in benzyl ether. Approximate values of hyperfine coupling constants were measured by interpolation using a linear field scan (Varian Fieldial), the end points of which were calibrated by proton NMR. The values in Gauss and our assignments are indicated as follows:



Steenken and co-workers⁶ have observed this radical at 0 and 30 °C with a similar photolytic method but with the reagents in benzene solution. Our coupling constants are in satisfactory agreement. Our assignment of the 1.35-G coupling is the same as that of Steenken and co-workers. The assignment of the meta hydrogens should then be made³ as shown. They appear inequivalent due to a lack of sufficiently rapid rotation of the phenyl about the bond to the carbon with high spin density. The coupling values next to the parentheses are unassigned. A pair go with the inequivalent hydrogens in the ortho position and one goes with the para position.

The conversion of 1 to 2 at higher temperatures was carried out with solutions in benzene for two reasons. First, with the use of neat ether the intense light caused a colored deposit to develop on the surface of the silica cell which reduced the optical transmission. Working in benzene solution eliminated this problem. Secondly, with neat ether extraneous signals appear from trace impurities. Extraneous signals were not observed in benzene solution except at relatively high temperatures where benzene participated in a reaction as noted later. The solution used in the temperature dependence work was 7.5% di-*tert*butyl peroxide and 10% benzyl ether in benzene. Tem-

⁽⁶⁾ Steenken, S.; Schuchmann, H.-P.; von Sonntag, C. J. Phys. Chem. 1975, 79, 763-4.



Figure 2. High- and low-field portions of spectra from the photolysis of 7.5% di-*tert*-butyl peroxide and 10% benzyl ether in benzene: (top) $C_{6}H_{5}\dot{C}H_{2}$; (bottom) $C_{6}H_{5}\dot{C}HOCH_{2}C_{6}H_{5}$; (center) mixed radicals. Arrows are described in the text.

peratures up to 200 °C were used with benzene solutions, well above the normal boiling point of benzene (80 °C). The pressure utilized (68 atm) was higher than the critical pressure⁷ of benzene (50.1 atm). The system was always present as a liquid phase since the temperatures were below the critical temperature (290.5 °C).⁷

The activation energy of the reaction given in eq 4 was determined by using the method of Hamilton and Fischer.⁸ Needed is the ratio of intensities of lines from 2 and 1, and in the present work well enough resolved lines appear only at the ends of the spectrum. Figure 2 shows the high- and low-field ends of interest. At 27 °C only lines of 1 appear, and two evaluations were made by using the second and fifth lines from the ends as indicated. Lines of 2 appear at 175 °C and no lines of 1 are observable, whereas at 130 °C lines from both radicals are present. One prominent line of 2 was very well suited for the measurements and is indicated in Figure 2.

Hamilton and Fischer⁸ presented a development with discussion, and here we sketch those parallel features peculiar to our situation. The relevant equations are

$$(CH_3)_3COOC(CH_3)_3 \xrightarrow{k_r} 2(CH_3)_3CO$$
(6)

$$(CH_3)_3C\dot{O} \xrightarrow{k_m} (CH_3)_2CO + \dot{C}H_3 \qquad (7)$$

$$(CH_3)_3C\dot{O} + C_6H_5CH_2OCH_2C_6H_5 \xrightarrow{\kappa_p} 6 \\ (CH_3)_3COH + C_6H_5\dot{C}HOCH_2C_6H_5 \quad (8)$$

$$\begin{array}{c} C_6H_5\dot{C}HOCH_2C_6H_5 \xrightarrow{R_7} C_6H_5CHO + C_6H_5\dot{C}H_2 & (4) \\ 1 & 2 \end{array}$$

$$i + j \xrightarrow{k_{ij}} \text{products} \quad (i, j = 1, 2, 3) \quad (9)$$

$$k_{ij} = 2(k_{ii}k_{jj})^{1/2}$$
 for $i \neq j$ (10)

The solution for steady-state irradiation is

$$\frac{[\mathbf{2}]}{[\mathbf{1}]} = \frac{k_{\rm r}}{2k_{22}^{1/2}(k_{\nu}[\mathbf{4}])^{1/2}} \tag{11}$$

As pointed out by Hamilton and Fischer,⁸ termination reactions should have activation energies of $\simeq 2 \text{ kcal/mol}$



Figure 3. High- and low-field portions of spectra obtained by photolysis at 200 °C: (top) methylcyclohexandlenyl from 7.5% di-*tert*-butyl peroxide in benzene; (bottom) mixture of methylcyclohexadlenyl and benzyl from 7.5% di-*tert*-butyl peroxide and 10% benzyl ether in benzene. Lines designated by asterisks are mentioned in the text.

and $k_{\nu}[4]$ should be essentially temperature independent which leads to

$$\log \frac{[2]}{[1]} = -\frac{E_{\rm r} - 1}{2.3RT} + \text{constant}$$
(12)

where E_r is the activation energy for eq 4 in units of kcal/mol. Note that Hamilton and Fischer⁸ defined quantities $I = k_p[5][6]$ and $J = k_m[5]$ from which it can be shown that the steady-state solution (eq 11) becomes

$$[\mathbf{2}]/[\mathbf{1}] = k_{\rm r}/(2k_{22}(I+J))^{1/2}$$
(13)

This differs from their expression presumably because of a typographical error. Final expressions (our eq 12) agree. In using eq 12 the ratio [2]/[1] may be replaced by line heights provided line widths do not change with temperature and E_r may be evaluated from the slope of an Arrhenius plot.

The high- and low-field counterparts of a given line (Figure 2) are of greatly different intensities. This is caused by dynamic spin polarization, and in our case the degree of polarization has a temperature dependence. A correction is made by taking the intensity of a line as the average of the high- and low-field counterparts. This method of correction is predicated on the polarization mechanism being the radical pair diffusion model.⁹

As indicated earlier, the rotation of the phenyl group of 1 is sufficiently slow that the pairs of meta and ortho hydrogens appear inequivalent. We have examined¹⁰ three benzylic radicals with similar inequivalences and found that the activation energy for rotation is approximately 13 kcal/mol. Line width changes associated with this activated rotation occur over the temperature range of 100–200 °C. We would expect 1 to behave similarly. In selecting the lines of 1 to be used (Figure 2) careful consideration was given to the $m_{\rm I}$ values in order to avoid these dynamic broadening effects.

Weak, extraneous lines are mixed with those from benzyl at higher temperatures, and the origin of these lines was studied. A pair are indicated with asterisks in the spectrum at 175 °C in Figure 2. At 200 °C the lines with asterisks become relatively more prominent as shown in the bottom part of Figure 3. At 200 °C there is a contribution to overall signal intensity from initiation by pyrolysis of the peroxide.³ In the top part of Figure 3 portions of a spectrum obtained by photolyzing 7.5% ditert-butyl peroxide in benzene are shown. Benzyl is not

⁽⁷⁾ Jordan, T. E. "Vapor Pressure of Organic Compounds"; Interscience: New york, 1954; p 19.

⁽⁸⁾ Hamilton, E. J., Jr.; Fischer, H. Helv. Chim. Acta 1973, 56, 795-9.

⁽⁹⁾ Ayscough, P. B.; Lambert, G. J. Chem. Soc., Faraday Trans. 1 1976, 72, 1770-81.

⁽¹⁰⁾ Conradi, M. S.; Zeldes, H.; Livingston, R. J. Phys. Chem. 1979, 83, 2160-1.



Figure 4. Arrhenius plots using ratios of signal intensities as a function of temperature. Line 2 (squares) and line 5 (circles) were used from the spectrum of $C_8H_5\dot{C}HOCH_2C_8H_5$, see text.

present. The radical has been identified as methylcyclohexadienyl (7) and approximate values of coupling con-



stants are $a(CH_3) = 0.55$ G, couplings for pairs of hydrogens of 8.65 and 2.8 G, and for single hydrogens of 40.8 and 12.65 G. The radical forms from the reaction of benzene with $\dot{C}H_3$ generated by eq 7. The evaluation of E_r was made at lower temperatures (105.0–154.8 °C), and no problem was encountered with the formation of 7. Moreover the temperature was low enough that initiation by pyrolysis of the peroxide was negligible.

Arrhenius plots are shown in Figure 4. A least-squares fit was made to the points. The slope evaluated from line 2 of 1 is -3140 and that from line 5 is -3210. From the average and from eq 12 the value of E_r is 15.5 kcal/mol. The estimated accuracy is $\pm 15\%$.

An order of magnitude estimate of k_r may be made from eq 11. At 130 °C (Figure 2) the value of [2]/[1] is 0.37 by taking account of spectral multiplicities and taking line widths for the two radicals equal. By extrapolating rate constants¹¹ for benzyl self-reaction in toluene we estimate k_{22} to be 9.5×10^9 M⁻¹ s⁻¹ at 130 °C. An estimate of k_p [4] can be made at 27 °C (Figure 2). At this temperature eq 4 does not participate, since spectral lines of 2 do not appear. Extrapolation of the Arrhenius plots (Figure 4) also show a negligible amount of 2 present. The steadystate solution of eq 6–10 gives

$$k_{v}[4] = k_{11}[1]^{2} + k_{33}[3]^{2} + 2k_{11}^{1/2}k_{33}^{1/2}[1][3] \quad (14)$$

An examination of the spectrum shows [3] negligible compared to [1], and to good approximation $k_{\nu}[4] = k_{11}[1]^2$. The approximate concentration of 1 at 27 °C (Figure 2) is 2.5×10^{-6} M. Unfortunately we do not have an experimental value for k_{11} . Typical values of $2k_t$ for self-reaction of α -substituted carbon radicals¹² are near 10⁹ M⁻¹ s⁻¹, and we use 5 × 10⁸ M⁻¹ s⁻¹ for k_{11} . This leads to an estimate of $k_{\nu}[4]$ of 3.1 × 10⁻³ M s⁻¹, and substitution into eq 11 gives an estimated value of k_{r} at 130 °C of 4 × 10³ s⁻¹. This leads to an estimate of the Arrhenius A factor of 1 × 10¹² s⁻¹.

Discussion

Several calculations can be made that are related to the free radicals found in the benzyl ether system. The equilibrium constant for the dissociation of bibenzyl to form benzyl¹³ is 0.75×10^{-10} M at 605 °C, and this extrapolates¹³ to 4.9×10^{-13} M at 497 °C. The concentration of bibenzyl formed from the pyrolysis of benzyl ether at 497 °C deduced from Table I is 7.4×10^{-3} M at room temperature or approximately 3.7×10^{-3} M at 497 °C when an estimate of the decrease in density is included. This leads to an equilibrium concentration of benzyl of $4.3 \times$ 10^{-8} M. The observed steady-state concentration is $3.0 \times$ 10^{-7} M. The observed benzyl was not at equilibrium with bibenzyl, but approximately 14% of the observed concentration of benzyl can be attributed to dissociation of bibenzyl which gives some help in sustaining the chain process.

The ESR measurements provide information on the mean lifetimes of the chain carriers appearing in eq 3-4. From the measurements of kinetic parameters for eq 4 the calculated value of k_r at 497 °C is 4×10^7 s⁻¹, giving a lifetime τ_1 of 1 of 2.5×10^{-8} s. A lower limit of the lifetime τ_2 of **2** in eq 3 may be deduced from the observed ESR line width (Figure 1). The peak-to-peak width on the derivative spectrum was found to be 0.07 G. Processes that shorten the lifetime of spin states including chemical lifetime produce an increase in ESR linewidth. A characteristic time T_2 derived from the line width can be calculated.¹⁴ If we take the line to have Lorentzian shape which is appropriate for our experimental conditions the value of T_2 from the observed line width is 9.4×10^{-7} s. This value of T_2 is typical of similar radicals where the chemical lifetime is not short enough to produce line broadening. Accordingly we attribute the value of T_2 to relaxation processes, and the value of τ_2 must be greater than 9.4 \times 10⁻⁷ s. The ratio of τ_2 to τ_1 is greater than 38 indicating that of the two reactions constituting the chain eq 3 is rate limiting. Moreover, the steady-state ratio of concentrations of the chain carriers [2]/[1] is in excess of 38. This implies that termination of the chain by radical-radical reactions will have very little contribution from 1 and will be almost exclusively through eq 5. An ESR spectrum of 1 could not be observed during pyrolysis, and this is now understandable because of its very small concentration. The short lifetime of 1 also affects the line width. From the value of τ_1 the lines would have a width of at least 2.6 G which further increases the difficulty of seeing a spectrum of 1 during pyrolysis. Pyrolytic experiments were carried out at temperatures down to 452 °C. At this temperature the value of τ_1 has increased to 4.7×10^{-8} s, but this is not sufficient to qualitatively alter the above conclusions, especially that eq 5 is the main pathway for chain termination. The scheme given by eq 1-5 is perturbed by decomposition of benzaldehyde which will be discussed later.

Another lifetime that may be calculated is that of benzyl in the chain termination reaction (eq 5). This is the mean

⁽¹²⁾ Ingold, K. U. "Free Radicals"; Kochi, J. K., Ed.; Wiley: New York, 1973; p 54.

⁽¹³⁾ Zeldes, H.; Livingston, R. Fuel 1982, 61, 1254-9.

⁽¹⁴⁾ See, for example, Wertz, J. E.; Bolton, J. R. "Electron Spin Resonance"; McGraw-Hill: New York, 1972.

lifetime of a chain. It is given by

$$\tau = \frac{[\mathbf{2}]}{\mathrm{d}[\mathbf{2}]/\mathrm{d}t} = \frac{1}{2k_{22}[\mathbf{2}]}$$
(15)

If we use a high temperature value ¹³ of $2k_{22}$ of 1.5×10^{10} M⁻¹ s⁻¹ and the observed value of [2] at 497 °C of 3.0×10^{-7} M the value of τ is 2.2×10^{-4} s. The mean time to complete the two reactions of the chain is $\tau_1 + \tau_2$, and the chain length is given by $\tau/(\tau_1 + \tau_2)$. With the values given above the kinetic chain length at 497 °C must be less than 230.

The scheme given by eq 1-5 implies a value of unity for the mole ratio of toluene to benzaldehyde. Schlosberg and co-workers¹ using a tubing bomb at 450 °C found this ratio greater than unity and showed that benzaldehyde decomposes at 450 °C. Values of this ratio from the analyses of Table I are 1.14, 1.06, and 1.035 at 497, 474, and 452 °C, respectively. The ratio approaches unity as required by stoichiometry. We have pointed out⁴ that pyrolyses carried out in the equipment used for this ESR work give a relatively small amount of burnup with greater emphasis to earlier products because of the short contact time at high temperature. We do not have suitable physical data for benzyl ether for an accurate calculation of residence time but can make an approximate evaluation. From the liquid pumping rate at room temperature and capillary diameter (0.146 cm) the transit time through the heated zone is approximately 5 s. At elevated temperatures this time will be reduced in proportion to the decrease in density, but with the conditions we have used it will be longer than 1.5 s as indicated by studies of other systems where we have suitable data. With a residence time of 6 min at 450 °C in a tubing bomb¹ the amount of benzyl ether remaining was 13% to be compared with our value of 89.3% at 452 °C (Table I). The mole ratio of toluene to benzaldehyde deduced from reported weight percentages was 2.35 in the bomb work¹ to be compared with our value of 1.035.

In principle the data of Table I may be used to calculate chain length where either the toluene or benzaldehyde yield is a measure of combined chain length, and either the benzyl alcohol yield is used as a measure of the number of chains initiated or bibenzyl used as a measure of the number of chains terminated. With regard to termination of the chain (eq 3-4) there is an important simplifying feature. As shown earlier, the mean lifetime of 1 is so short that it does not sensibly contribute to chain termination. This means that, in principle, the one termination product, bibenzyl, is a measure of termination.

In practice there is some pyrolysis of benzaldehvde as indicated by the mole ratios of toluene to benzaldehyde presented above. It appears that toluene remains a good measure of combined chain length, and the situation looks particularly favorable at the lowest temperature, 452 °C, where even the benzaldehvde vield could be used with relatively little error incurred. The situation for deducing the number of chains is less favorable. The stoichiometry of eq 1-5 requires the initiation of two chains for each molecule of benzyl alcohol that is formed and the termination of two chains for each molecule of bibenzyl. The mole ratio of benzyl alcohol to bibenzyl should be unity. The values calculated from Table I are 2.81, 1.49, and 0.60 at 497, 474, and 452 °C, respectively. The values at the two higher temperatures are significantly greater than unity and well outside the limits of accuracy of the assays. We regard this departure from unity as a perturbing effect from thermal decomposition of benzaldehyde. For example, radicals formed from benzaldehyde could participate both as chain initiators and chain terminators. The above ratios should approach unity in the low temperature limit. The value at 452 °C has fallen below unity, but here the amounts of the two substances are very small (Table I) and the analytical accuracy has severely deteriorated. The estimated accuracy for bibenzyl at 452 °C is ±10% while that of benzyl alcohol is very much poorer because of its smaller amount on a weight basis and a large correction for the benzyl alcohol present as an impurity in the initial benzyl ether. The only chain length calculation we feel is reliable is at 452 °C using bibenzyl as a measure of chains terminated. The molalities of toluene and bibenzyl calculated from Table I are 0.531 and 0.00187, respectively. These lead to a chain length at 452 °C of 140. This is a long chain. Despite the strong perturbing effect of decomposition of benzaldehyde at higher temperatures it appears that the chain length becomes smaller with increasing temperature and at 497 °C is well under the upper limit of 230 found kinetically.

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