

Kinetics and Pressure Effect in the Thermolysis of Liquid Bibenzyl

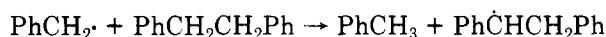
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The rate of thermolysis of liquid bibenzyl to toluene and stilbene has been measured as a function of temperature and pressure with upper limits of 400 °C and 1000 atm (101 MPa). The activation parameters are $E_{\text{act}} = 63$ kcal, $S_{\text{act}} = +9$ eu, and $V_{\text{act}} = +31$ mL. They are consistent with a rate-controlling step involving formation of a widely separated pair of benzyl radicals. The V_{act} is interpreted in the light of cage effects, and the conventional treatment of diffusive separation and recombination of radical pairs as activated processes is called into question.

The thermolysis of bibenzyl is a reaction of considerable theoretical and practical importance. Its activation energy gives a measure of the heat of formation and the stabilization energy of the benzyl radical. The rate is measurable at temperatures near 400 °C, which makes it susceptible to study by techniques which would not be feasible for reactions involving C-C bond fission without stabilization. It becomes reactive at about the same conditions used for hydrogenation, solvent extraction, and thermolysis of coal and has been used as a model compound in studies of these reactions.¹⁻⁴ The products of decomposition are toluene, stilbene, benzene, styrene, phenanthrene, and small amounts of ethylbenzene, diphenyl, diphenylmethane, and fluorene.^{5,6} At low temperatures the chief products are toluene and stilbene. The sequence of steps in the reaction may be represented as follows:



Apparently the only reported kinetic study up to the present is the 1951 paper of Horrex and Miles.⁵ Their measurement of the temperature dependence of the rate in the vapor phase gives a preexponential factor of $10^{9.3}$ which implies an activation entropy of -20 eu. It is now generally agreed that the preexponential factor should have a value in excess of 10^{13} for dissociative formation of a pair of polyatomic radicals.⁷ For the closely related decomposition of toluene to H and $\text{PhCH}_2\cdot$, a value of $10^{14.8}$ has been found.⁸ Madison and Roberts⁹ report a semiquantitative treatment of the thermolysis of bibenzyl in the liquid phase in borosilicate tubes with a much lower temperature (475 vs. 630-770 °C) and a longer time (1800 s vs. 0.17-0.18 s). Their data yield an estimate of rate which is 2 orders of magnitude greater than would be predicted by the reported activation parameters. Clearly, a new quantitative study is warranted.

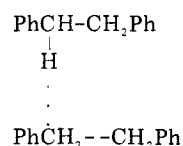
Our chief interest in investigating the kinetics of the liquid-phase thermolysis was to determine the effect of hydrostatic pressure on the rate and to evaluate the ac-

tivation volume. This approach to the characterization of transition states has had wide application in recent years. The major findings and their interpretations have been reviewed by Asano and le Noble.¹⁰ A review by Neuman¹¹ deals specifically with homolytic reactions. The appeal of the method arises from the possibility of comparing the volumes of transition states with those of stable substances in order to estimate the relative position of the transition state on the reaction coordinate.

All of the activation volumes for reactions in the liquid phase which have been reported up to the present have a temperature ceiling of 200 °C. We were especially interested to see whether it would be feasible to extend the limit to 400 °C and thereby gain access to a large group of pyrolytic reactions whose mechanisms are difficult to study by conventional methods. The main difference we anticipate at the higher temperature is that most liquids will be expanded by 30-40% above their normal volumes. This will increase the free volume more than threefold and should greatly magnify the contribution of free volume to the volume of transition states in which bond breaking or formation is far advanced.

Results and Discussion

Kinetic Order. At the outset it appeared that the reaction was much faster in the liquid phase than would be predicted by the activation parameters reported for the vapor phase.⁵ It seemed possible that in the liquid phase the reaction might become bimolecular as shown:



A bimolecular process involving neutral molecules is expected to show an acceleration with pressure, which is contrary to what we find. An ionic mechanism would lead to an acceleration by pressure regardless of kinetic order and can be rejected with even greater confidence. As a further test we measured the rate of reaction of a solution containing 25% bibenzyl and 75% biphenyl. The rate constant at 400 °C and 6.7 MPa with 10% completion was $1.58 \times 10^{-5} \text{ s}^{-1}$ whereas for pure bibenzyl it was 1.50×10^{-5} . Because of the accumulation of byproducts, it was not considered worthwhile to follow the reaction to a high degree of completion.

Wall Effects. For measuring reaction rates at high temperatures it is necessary and often difficult to guard against adventitious catalytic effects particularly by the walls of the reaction vessel. A search of the current lit-

(1) C. J. Collins, V. F. Raaen, B. M. Benjamin, and G. W. Kabalka, *Fuel*, **56**, 107 (1977).

(2) D. P. Mobley, S. Salim, K. I. Tanner, N. D. Taylor, and A. T. Bell, *Prepr., Div. Pet. Chem., Am. Chem. Soc.*, **23**(4) (1978).

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(8) S. J. W. Price, *Can. J. Chem.*, **40**, 1310 (1962).

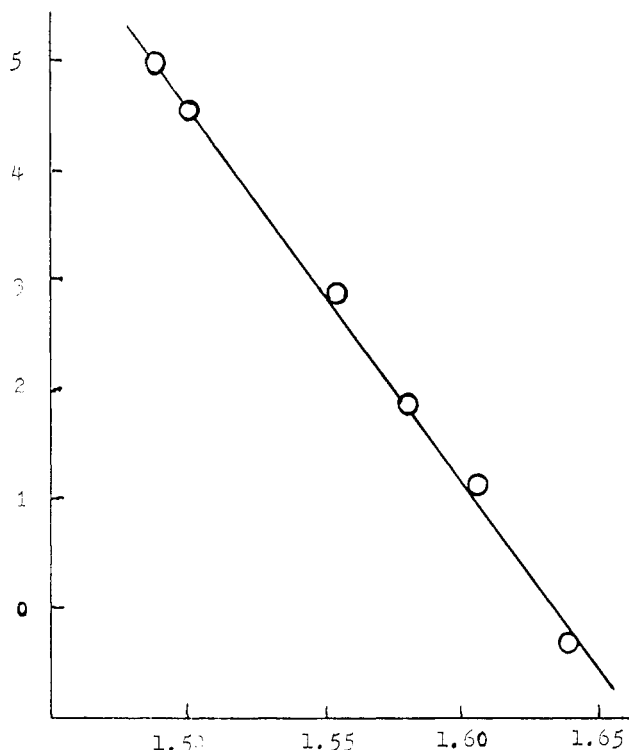
(9) J. J. Madison and R. M. Roberts, *Ind. Eng. Chem.*, **50**, 237 (1958).

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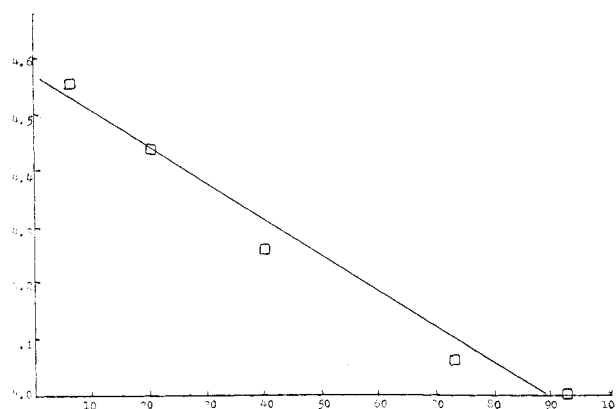
Table I. Reaction Rate Constants

		P = 6.7 MPa				
T, K	673	668	644	633	623	610
10 ⁷ k, s ⁻¹	148	95	19	6.7	3.2	0.73
		T = 668 K				
P, MPa	6.7	20	40	73	93	
10 ⁷ k, s ⁻¹	95	85	71	58	55	

Figure 1. Plot of $10^7 \ln k \text{ s}^{-1}$ vs. $10^3(1/T)$.

erature on rate measurements for coal conversion and other fuel-related reactions at elevated temperature and pressure did not furnish a description of any apparatus in which the reaction mixture is protected from transition metals. A previous study in this laboratory encountered difficulty with catalysis by stainless steel and led to the use of externally pressurized sealed glass tubes up to about 4 MPa.¹² In the present study it was found that samples could be confined in ordinary glass syringes with the tips sealed off and pressurized to 100 MPa at 400 °C with very little interchange of material with the pressurizing fluid. The syringes can be used repeatedly without deterioration and without any so-called conditioning effect on thermolysis of bibenzyl. There is still the possibility of catalysis by glass to be considered, so we added powdered borosilicate glass to one sample until the liquid was almost entirely contained in the interstices. An analytical sample was taken from the bottom to ensure maximum exposure to glass surface. There was no increase in rate.

Activation Parameters. Table I lists reaction rates for various temperatures from 337 to 400 °C and pressures from 6.7 to 93.3 MPa. Figures 1 and 2 are plots of $\log k$ vs. $1/T$ and P , respectively. The slopes give values of $63 \pm 2 \text{ kcal}$ for the activation energy (E_{act}) and $+31 \pm 5 \text{ mL}$ for the activation volume (V_{act}). The preexponential factor is $10^{15.5}$ which is nearly the same as the value of $10^{14.8}$ reported for the thermolysis of toluene.⁸ The activation entropy, calculated from the relation $10^{15.5} = (kT/h) \exp[(S_{\text{act}} + R)/R]$, is 8.8 at 673 K. For ethane the E_{act} for

(12) K. R. Brower, *Fuel*, **56**, 245 (1977).Figure 2. Plot of $10^7 \ln k \text{ s}^{-1}$ vs. P in MPa.

C-C bond breakage in the vapor phase is 88 kcal⁷ from which it would appear that the decrease to 63 kcal for bibenzyl corresponds to a stabilization energy of 12–13 kcal for the benzyl radical. Comparison of the E_{act} for C-H bond breakage in toluene (85 kcal) and methane (104 kcal) gives a substantially larger estimate of 19 kcal, but if comparison is drawn to ethane instead (98 kcal), the stabilization energy is 13 kcal.⁷ The direct comparison of activation parameters for our relatively slow and cool liquid-phase reaction with those of the much hotter gas-phase reactions of ethane and toluene could prove to be unjustified because the state of aggregation does have an effect on the heat capacities of all equilibria. On the other hand, if the benzyl radicals really were stabilized by 19 kcal and the E_{act} were 50 kcal ($88 - 2 \times 19$), the S_{act} would be negative, which seems unlikely. For reasons which were not stated, O'Neal and Benson¹³ adopted a value of 13 kcal for the stabilization energy of the benzyl radical which is needed in the process of calculating its entropy and heat capacity. Their results are $S^\circ = 75.6 \text{ eu}$, $C_p^\circ(300 \text{ K}) = 25.4 \text{ cal mol}^{-1} \text{ K}^{-1}$, and $C_p^\circ(500 \text{ K}) = 40.1 \text{ cal mol}^{-1} \text{ K}^{-1}$. Elsewhere¹⁴ they estimate the corresponding properties of bibenzyl to be $S^\circ = 129.9 \text{ eu}$, $C_p^\circ(300 \text{ K}) = 44.08 \text{ cal mol}^{-1} \text{ K}^{-1}$, and $C_p^\circ(800 \text{ K}) = 85.98 \text{ cal mol}^{-1} \text{ K}^{-1}$. These values give $S_{\text{act}} = +21.3 \text{ eu}$ and $\Delta C_p(300 \text{ K}) = +6.7 \text{ cal mol}^{-1} \text{ K}^{-1}$. The values for the liquid phase may be significantly different, but it is most unlikely that they have different signs.

Our chief interest in the kinetics of thermolysis of bibenzyl was to find and interpret V_{act} for which our value is $+31 \pm 5 \text{ mL}$. For single-bond homolyses in the liquid phase under ordinary conditions V_{act} is invariably positive but considerably smaller.¹⁰ The only directly comparable measurement is on the vapor-phase decomposition of ethylcyclobutane¹⁵ at 410 °C for which V_{act} is reported to be $+28 \text{ mL}$. The rate effect and pressure range for this measurement were smaller than usual because the pressure was generated by adding nitrogen from a cylinder. The mechanism of this reaction is unknown. A more closely related reaction is the racemization of benzyl *p*-tolyl sulfonide¹⁶ which is believed to proceed by way of the radical pair $\text{PhCH}_2 \cdot \text{SO}-p\text{-tol}$. One of the strong pieces of evidence is that bibenzyl is found among the products. The V_{act} for this reaction is $+26 \text{ mL}$ at 141 °C.¹⁷ It thus appears that homolyses at high temperature have exag-

(13) H. E. O'Neal and S. W. Benson, "Free Radicals", Vol. II, Jay Kochi, Ed., Wiley-Interscience, New York, 1973, p 330.

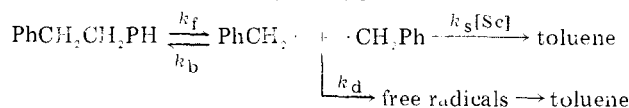
(14) S. W. Benson et al., *Chem. Rev.*, **69**, 279 (1969).(15) J. Aspden, N. A. Khawaja, J. Reardon, and D. J. Wilson, *J. Am. Chem. Soc.*, **91**, 7580 (1969).(16) E. Miller, D. Rayner, H. Thomas, and K. Mislow, *J. Am. Chem. Soc.*, **90**, 4861 (1968).(17) K. R. Brower and T. Wu, *J. Am. Chem. Soc.*, **92**, 5303 (1970).

gerated positive activation volumes. It has been suggested by Asano and le Noble¹⁸ that "expansion volume" (free volume) makes a major contribution to V_{act} for nearly nonpolar reactions such as the one reported here. Although it is not convenient to measure the density of bibenzyl at 400 °C, we have two ways of estimating its expansion. The relative volume of petroleum hydrocarbons of similar boiling point at 400 °C and 7 MPa is approximately 1.38 and is not very sensitive to paraffinic or nonparaffinic character.¹⁹ We also measured the relative volume of our pressurizing fluid (biphenyl/diphenyl ether eutectic) by cooling the sealed pressure vessel from 400 °C and 7 MPa and measuring the volume of the void. The result is 1.33. We estimate the free volume of the benzyl radical to be 35% of the molar volume of toluene under room conditions which is therefore about 37 mL. The value of 31 ± 5 mL for V_{act} consequently suggests that the development of free volume by a pair of benzyl radicals in the transition state is about 50% complete. It is probably not appropriate to think of such a voluminous radical pair as "caged".

Cage Effects. Reactions initiated by homolytic formation of radicals in solution are often accompanied by cage effects which is to say that the radical pair may interact by recombining with isomerization or racemization or by disproportionating before either radical has a chance to break out of the cage formed by surrounding solvent molecules. This complex subject has been critically reviewed by Koenig and Fischer.²⁰ The special relation of cage effects to pressure effects has been discussed by Neuman.¹¹ The features of the thermolysis of bibenzyl which place it in context among such reactions are that it has no intervening molecule such as N_2 in the decomposition of azo compounds or hyponitrites and that the radicals are consumed primarily by scavenging with bibenzyl itself as the hydrogen-donating scavenging agent. The absence of an intervening molecule increases the probability of recombination of a radical pair which in principle might have been sufficiently separated to permit some form of molecular reorganization. This has a bearing on the interpretation of V_{act} which will be discussed below. It seemed conceivable that the geminate benzyl radicals could recombine with isomerization perhaps to a nuclear substituted benzyltoluene, so we reacted a sample beyond 50% completion and collected all material which was eluted from a gas chromatographic column between styrene and stilbene. The NMR spectrum of this material showed only the sharp singlet of bibenzyl outside of the aromatic region. Not more than 1% of benzyltoluene or any other structural isomer could have formed. Langhals and Fischer²¹ have reported that benzyl radicals generated by low-temperature photolysis of dibenzyl ketone produce up to 19% of combined isomers of benzylmethylenecyclohexadiene as unstable intermediates which ultimately form the favored coupling product, bibenzyl. The yield of intermediates seems to have a maximum at 28 °C. It is possible and even likely that they were formed without detection in our experiments, but the amounts could be very small if the reported temperature variation holds over the large interval from 62 to 400 °C.

Cage effects are sometimes analyzed quantitatively by measuring the ratio of combination products to scavenged

Scheme I



products as a function of scavenger concentration. The key concept is that scavengers in low concentration only react with free radicals whereas at higher concentration they intercept pairs which are not completely separated. Since the recombination of benzyl radicals to bibenzyl is not observable, we are restricted to observing changes of rate rather than product ratios. In Scheme I we see how the rate of formation of toluene is governed by the rate constants for generation and recombination of benzyl radicals (k_f and k_b), the rate constant for diffusive separation (k_d), and the rate of scavenging of pairs ($k_s[\text{Sc}]$) which is assumed to be proportional to scavenger concentration ($[\text{Sc}]$). In the experiment described in the section on kinetic order we reduced the concentration of scavenger, bibenzyl itself, by a factor of 4 by dilution with biphenyl. The rate of formation of toluene per mole of bibenzyl was not reduced. Either $k_s[\text{Sc}]$ is negligible or it dominates k_b and k_d at both concentrations of Sc. The latter does not seem very likely because k_s should be increased by pressure, thus giving V_{act} a near-zero value. In a further experiment we added a high concentration of tetralin (50% by weight) which is a more effective scavenger. It completely suppresses the formation of the product of scavenging by bibenzyl which is stilbene. The rate was not increased, and again we are forced to conclude that no significant fraction of radical pairs is intercepted by scavenging. The fate of these pairs is determined by a competition between k_b and k_d which could be one-sided. If k_d is rate controlling, then the formation of caged radicals is a preequilibrium process, and the interpretation of activation parameters is straightforward because they are not composite quantities.^{11,20} If k_f alone is rate controlling, then we cannot consider the reacting bond to be sufficiently broken to permit any kind of molecular reorganization until the free volume has increased by 30 mL. This does not seem likely since cage reactions have been found to compete with free-radical products in cases where the apparent V_{act} is much smaller.¹¹ We are thus obliged to consider the possibility that k_b and k_d compete in the consumption of radical pairs and that the activation parameters are not properties of any well-defined species.

A factor of possible significance is the viscosity of the reaction mixture at 400 °C which is probably unusually low. Direct measurement would be difficult, but it is possible to estimate the viscosity by means of the relation $1/\eta = B(V/V_0 - 1)$, which Hildebrand²² has found to correlate the viscosities of nonassociated liquids over very wide ranges of temperature and pressure. The constant B has only a short range of variability, and some typical values in cP^{-1} are as follows: 15.0, toluene; 16.1, decane; 10.5, decalin; 11.1, hexadecane. The intrinsic volume, V_0 , is found by extrapolating a plot of $1/\eta$ vs. V to zero fluidity. At room temperature it is usually 5–10% less than the molar volume, the molecular weight divided by the density. By assuming $B = 10$ for bibenzyl and a factor of 1.35 for the expansion from room temperature to 400 °C and 7 MPa as discussed above, we can estimate the $V/V_0 - 1 = 0.4$ and $\eta = 0.25$ cP. This viscosity is less than that of almost all solvents used in studies of cage effects and would tend to favor separative diffusion over recombination.²⁰

(18) T. Asano and W. J. le Noble, *Rev. Phys. Chem. Jpn.*, **43**, 82 (1973).

(19) J. B. Maxwell, "Data Book on Hydrocarbons", Van Nostrand, Princeton, NJ, 1950.

(20) T. Koenig and H. Fischer, "Free Radicals", Vol. I, Jay Kochi, Ed., Wiley-Interscience, New York, 1973, p 157.

(21) H. Langhals and H. Fischer, *Chem. Ber.*, **111**, 543 (1978).

(22) J. H. Hildebrand, "Viscosity and Diffusivity", Wiley-Interscience, New York, 1977.

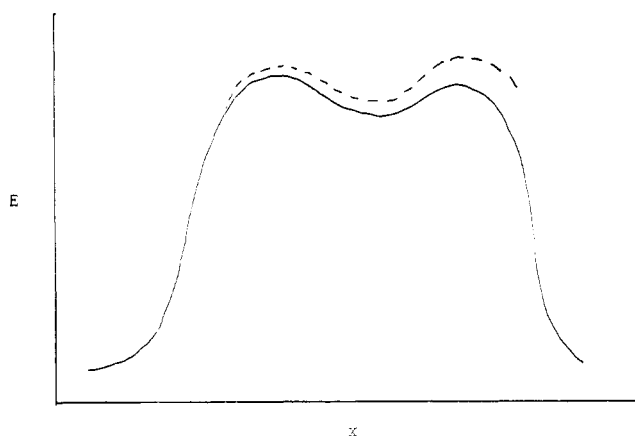


Figure 3. Plot of potential energy vs. reaction coordinate.

Interpretation of V_{act} in the Light of Cage Effects. The conventional formal treatment of k_f , k_b , and k_d as concurrent activated rate processes may tend to obscure the energetic and volumetric relationships and very likely is not even physically correct as we shall attempt to show. It is well-known that the barriers to recombination of radicals and also to diffusion are almost negligibly low in comparison to the free energy of activation for most reactions. We can represent the potential-energy diagram for the thermolysis of bibenzyl by Figure 3. The curve has a broad plateau with perhaps a shallow minimum at the value of x corresponding to the geminate radicals. Volume increases monotonically from left to right at least up to the point at which the radicals are equally likely to recombine or abstract hydrogen. The effect of pressure is to shift the curve upward by an amount which increases toward the right as shown by the dashed line. The effect is exaggerated for the sake of clarity. The value of the PV product at 100 MPa with $V_{act} = 30$ mL is 0.7 kcal, which is comparable to the depth of the energy minimum. In this special case there may be a significant effect of pressure on the geometry of the "transition states" for k_b and k_d . Benson and Berson²³ have argued that the effect is not observable for reacting bonds with force constants greater than 10^4 dyn/cm, but it seems likely that in this case the force constant could be less than 10^3 . The manifestation would be a decrease of V_{act} with pressure which is suggested by Figure 2. Demonstration of the effect with certainty would require temperature control within 0.3 K and analyses good to 2% which we are not presently able to achieve.

The difficulty with treating k_b and k_d as reaction rate constants which obey the relations $d \ln k/d(1/T) = -E_{act}/R$ and $d \ln k/dP = -V_{act}/RT$ is that diffusion is probably not an activated process, and recombination of radicals may also be nonactivated. Hildebrand and Alder²⁴ have shown that nonexponential equations with V as the primary variable are superior for predicting the effects of temperature and pressure on viscosity and diffusivity and have argued that it is not physically realistic to postulate that flow requires energy of activation. If this point is conceded, it is somewhat artificial to assign values of V_{act} to the diffusive separation and recombination of radicals.

Whether or not one attempts a dissection of what might be called the observed or apparent V_{act} into components associated with k_f , k_b , and k_d , the nature of the pressure effects is fairly clear. Application of a pressure of 100 MPa

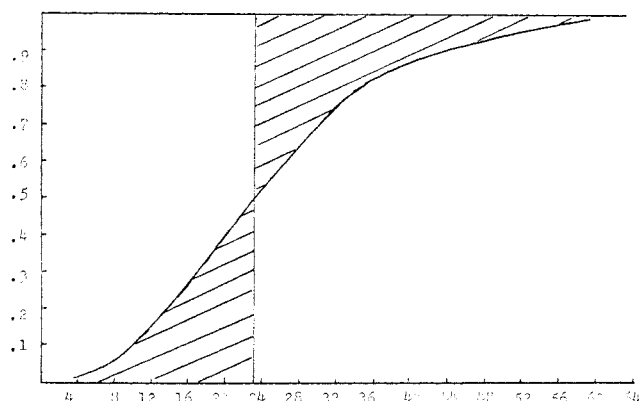


Figure 4. Plot of Q vs. t in min.

to ordinary liquids more or less doubles the viscosity and halves the diffusivity. Without question this should favor the return of geminate radicals to starting material over separation to give the final product. It is perhaps permissible, though it may not be strictly correct, to interpret this by saying that V_{act} for return is about -5 mL and V_{act} for separative diffusion is about $+10$ mL. An interpretation which is simpler and equally defensible is to say that the apparent V_{act} for the formation of toluene is the difference in volume between the reactant and the "point of no return" on the reaction coordinate in Figure 3. Taking into account the known effects of pressure on dissociative equilibria and diffusion, we should expect the rate of formation of toluene to be markedly reduced by pressure, which is equivalent to predicting a large positive apparent V_{act} . Consideration of the energy relationships in Figure 3 leads us to expect the "point of no return" will lie near the middle of the plateau with a development of free volume which is about 50% complete. The final conclusion is that formation of toluene requires a productlike "transition state" or "point of no return".

Experimental Section

Materials. Bibenzyl, biphenyl, and tetralin were obtained from Eastman Organic Chemicals. The pressurizing fluid is a eutectic mixture of biphenyl and diphenyl ether to which sufficient motor oil is added to depress the melting point to 25°C at 100 MPa.

Analysis of Reaction Mixtures. The ratio of toluene to unreacted bibenzyl was determined by gas chromatography at a column temperature of 200°C . Optimum sensitivity of peak-height ratio to composition occurred at about 12% conversion (6% toluene). Known mixtures were used for calibration in every run. Other peaks in the gas chromatogram were caused by benzene, styrene, and stilbene. The yield of stilbene appeared to be commensurate with the amount of toluene but could not be determined accurately. The ratios of benzene/toluene and styrene/toluene were both near 0.04. Analyses were reproducible within 5%.

Handling of Reaction Mixtures. The reaction cell is a 5-mL glass syringe with the metal tip removed and the bottom converted to a test-tube end. A 1-g sample of reactant or reaction mixture is placed in the barrel, and a plunger with the top sawed off is placed loosely in the opening. The assembly is heated above the melting point of the contents and quickly placed in a vacuum chamber. After the air has escaped, the vacuum is released, and the plunger enters the barrel. The filled cell is placed in an Aminco Micro Series reactor with a 1-in. bore which is then filled with pressurizing fluid. The reactor is connected to a hydraulic pump and placed in the thermostat which is described below. The temperature is raised toward the control point at $7-8^\circ\text{C}/\text{min}$. When the temperature is safely above the melting point of the sample, the outlet is closed, and pressure is controlled by releasing hydraulic fluid as required. Pressures below 1000 psi (6.7 MPa) are not used in order to be certain that there is no vapor space in the cell. We also wished to avoid the region of high initial

(23) S. W. Benson and J. A. Berson, *J. Am. Chem. Soc.*, **86**, 259 (1964).

(24) B. J. Alder and J. H. Hildebrand, *Ind. Eng. Chem. Fundam.*, **12**, 387 (1973).

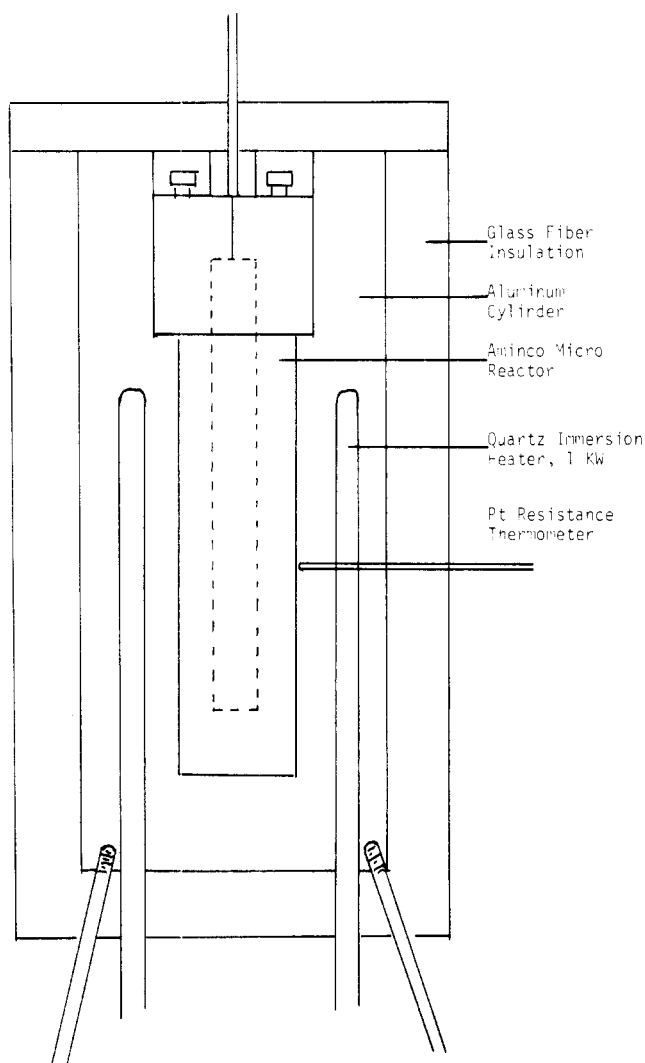


Figure 5. Apparatus used to heat pressure vessel.

compressibility. The time of attainment of the control temperature is noted and converted to an equivalent starting time as described below. Pressure adjustments are made during the next 0.5 h. After a suitable time (1 h minimum) the reactor is lifted clear of the thermostat and cooled at an initial rate of 15 °C/min (from 400 °C) by a blower. Throughout the cooling period the

pressure is maintained at 6.7 MPa or higher by pumping. When the cell has been removed from the reactor, the plunger can easily be pulled out against atmospheric pressure.

Determination of the Equivalent Starting Time. After the thermostat has reached the control temperature, the inner temperature of the reactor can be monitored by means of the pressure rise by using measured values of $(\partial T/\partial P)_V$. For our apparatus the derivative has values of 3.7 and 2.1 °C/MPa at 350 and 260 °C, respectively. It has been found that the rate of change of temperature with time is given by eq 1 in which T' is the control

$$\frac{T' - T}{T' - T_0} = e^{-kt} \quad (1)$$

temperature and T_0 is the temperature when $t = 0$. Substitution in the Arrhenius equation gives the ratio, Q , of the rate constants at T and T' as shown in eq 2. The equivalent starting time, t_0 ,

$$Q = \exp \left[\frac{E_{\text{act}}}{R} \left(\frac{1}{T'} - \frac{1}{T' - (T' - T_0)e^{-kt}} \right) \right] \quad (2)$$

is defined by eq 3. The amount of reaction which has occurred

$$\int_0^{t_0} Q dt = \int_{t_0}^{\infty} (1 - Q) dt \quad (3)$$

before t_0 is set equal to the deficiency of reaction beyond t_0 , and thus the amount of reaction at time t is the same as though the reaction had reached T' at t_0 . It is always possible to make the reaction slow enough to justify the assumption that only a small percentage of reaction has occurred up to about $2t_0$. For the thermolysis of bibenzyl at 400 °C the values of the constants are $T_0 = 320$ °C, $k = 1.5 \times 10^{-3} \text{ s}^{-1}$, and $E_{\text{act}} = 63$ kcal. Figure 4 gives Q as a function of t in minutes. The equated integrals of preceding eq 3 are represented by the shaded areas. The probable error in t_0 is about 1 min. We therefore use minimum reaction times of 1 h.

Thermostat. The pressure vessel is heated by the apparatus shown in Figure 5. Two pairs of 1-kW quartz heaters are wired in series to provide 4-kW at 230 V and 1-kW at 115 V. It is also possible to disconnect one pair to provide control heat at 0.5 kW. At 400 °C the power dissipation is about 0.35 kW. The reactor is lowered into the cavity by means of a coil of flexible pressure tubing, and the assembly is brought up to control temperature at 7–8 °C/min. The bandwidth of the controller is ± 1 °C. Temperature variations within the reactor can be followed by the pressure gauge. Throughout one cycle of the controller the temperature change is less than 0.15 °C and over several hours it is not more than 1 °C. Temperatures were calibrated at the melting points of zinc and lead.

Registry No. Bibenzyl, 103-29-7.

Conformational Preference of the Trimethylstannyl Group

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The conformational preference of the trimethylstannyl group in (trimethylstannyl)cyclohexane has been determined through analyses of *cis*- and *trans*-1-methoxy- d_3 -4-(trimethylstannyl)cyclohexane by ^1H NMR spectroscopy. The chemical shift of the equatorial trimethylstannyl protons has been shown to be upfield of the axial protons. The A value for the trimethylstannyl group is 0.94 ± 0.03 kcal/mol. It is demonstrated that the A values of the methoxy- d_3 and the trimethylstannyl groups are approximately additive.

A recent report by Kitching¹ and others on the stereochemistry of substitution reactions of the trimethylstannyl anion with cyclohexyl derivatives relied heavily upon ^{13}C

chemical shifts and ^{13}C - $^{117,119}\text{Sn}$ coupling constants to establish the conformation of reaction products. Some evidence from ^1H NMR spectroscopy was also observed, but it was inconclusive. The ^{13}C NMR spectral evidence was interpreted on the basis of previous ^{13}C work done by Kitching² in determining the A value of the trimethyl-

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