value for E_t and the calculated value for σ_L. It is also possible, using the preceding equations, to predict the slope of the middle segment and of the segment at high energy (Fig. 1) from values of the parameters obtained from the observed value for the intercept of the middle segment (Fig. 1) and for the intercept and the slope of the segment at low energy (Fig. 2); these predicted slopes may be compared to those observed. The calculated and observed values for the ten ion-molecule reactions studied are summarized in Table III. The values for the slopes agree very well, while the observed cross section [σ_K, obsd. = 82 $\pm$ 9Å.^{2}] is higher than the one estimated [σ_K, calcd. = 51Å.^{2}]. This disagreement is not very significant since the estimated value is highly arbitrary. It is significant that σ_K, obsd is practically constant, as required for a common molecule and very similar primary ions, although values of Q vary greatly.

The Free Radical, High Pressure Polymerization of Ethylenes. The Effects of Initiator Concentration, Monomer Concentration and Pressure on the Polymerization Rate[1]

BY ROBERT O. SYMCOX[2] AND PAUL EHRLICH

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The polymerization of ethylene, initiated by di-t-butyl peroxide, was studied in the presence of propane at 129° and at 750 to 2500 atm. The reaction is $^1/_2$ order over a more than 100 fold variation in initiator concentration and between first and second order in monomer. The logarithm of the polymerization rate and of the over-all rate constant are proportional to the pressure as in the polymerization of styrene. The pressure coefficient of the rate is smaller than that reported in other studies with ethylene. The difference is attributed to the fact that the present study was carried out under homogeneous conditions and that special care was taken to exclude oxygen. The application of the transition state theory to nonideal supercritical systems is discussed, and it is concluded that, to a first approximation, it should be possible to interpret the pressure coefficient of the polymerization rate in terms of a volume of activation which is found to equal −20 to −23 cc./ mole. Using literature data for the rate of initiator decomposition, values of $k_p/k_t^{1/2}$ are found to be higher, but within about an order of magnitude of those reported near atmospheric pressure.

Introduction

There is general agreement that our understanding of the kinetics of the free radical high pressure polymerization of ethylene is rudimentary; indeed, kinetic data on gas phase reactions of non-ideal gases at high pressures are scarce. Consequently, no theory for the interpretation of the kinetics of such reactions has been firmly established. There has been some question, for instance, whether the transition state theory, as ordinarily employed to interpret the effect of pressure[3,4] on liquid phase polymerizations[5,6] can be extended to ethylene in a straightforward manner.[7]

It was the purpose of this work to study the free radical initiated polymerization of ethylene at pressures up to several thousand atmospheres and under conditions where a kinetic analysis could be attempted. In particular, it was desired to obtain values of the rate constants for propagation and termination $(k_p/k_t^{1/2})$ valid in the high pressure region and to determine and interpret the effect of pressure on this ratio.

A previous study carried out in this laboratory[8] had demonstrated that traces of oxygen, in the parts per million range, could affect strongly and sometimes dominate the kinetics, in particular the pressure coefficient of the polymerization rate. The initiating mechanism by oxygen was shown to be of the branching chain type and therefore complex and not describable by a single rate constant. In addition, evidence has accumulated recently that nonideality renders the monomer, although a gas, a solvent for the polymer, but that the mutual miscibility of the two components depends strongly on the pressure.[9] In order to determine the effect of pressure on the rate constants under conditions where a generalization of the results to gaseous systems at high pressures might be permissible, it seemed therefore necessary to meet at least the two following conditions: initiation of the polymerization at known and reproducible rates where co-initiation by oxygen was negligible and operation under single-phase conditions. This was apparently accomplished by initiating with di-t-butyl peroxide under rigid control of oxygen at a temperature where the initiation rate of the latter was not excessive and by addition of propane, a better solvent for polyethylene than its monomer.[9]

Experimental

Reactor and Preparation of Reaction Mixture.—The reactor design, principle of carrying out the rate measurements, and method of filling with ethylene and propane were essentially as described for pure ethylene[8,10]. The pres-

(1) Presented in part at the 139th Meeting of the American Chemical Society, St. Louis, Missouri, March 1961.

(2) Monsanto Chemicals Ltd., Newport, Monmouthshire, England.

(3) M. G. Evans and M. Polanyi, *Trans. Faraday Soc.*, **31**, 857 (1935).

(4) S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw–Hill Book Co., New York, N. Y., 1941.

(5) C. Walling, "Free Radicals in Solutions," John Wiley and Sons, New York, N. Y., 1957, Chapter 5.

(6) S. D. Hamann, "Physico-Chemical Effect of Pressure," Butterworths, London, 1957.

(7) R. K. Laird, A. G. Morrell and L. Seed, *Discussions Faraday Soc.*, **22**, 126 (1957); see also E. Hunter in A. Renfrew and P. Morgan, "Polythene," Iliffe and Interscience Publishing Co., New York, N. Y., 1960.

(8) P. Ehrlich and R. N. Pittilo, *J. Polymer Sci.*, **43**, 389 (1960).

(9) P. Ehrlich and E. B. Graham, *ibid.*, **45**, 246 (1960).

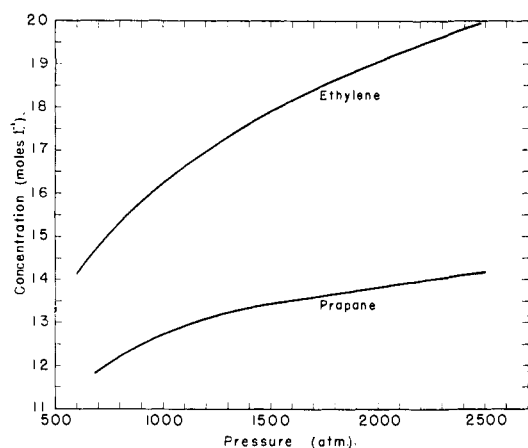(10) P. Ehrlich, J. D. Cotman, Jr., and W. F. Yates, *ibid.*, **24**, 283 (1957).

Fig. 1.—Concentration of pure ethylene and of pure propane vs. pressure at 130°.

ent reactor was a 2 foot piece of stainless steel tubing, 5/16″ i.d. × 9/16″ o.d., and 32 cc. volume, 1.5 cc. of which were "dead volume" maintained close to room temperature.[8] Some of the physical arrangements were slightly different from those of the previous study. In particular, stirring throughout the entire reaction was maintained by allowing a coil of Teflon-insulated wire which surrounded the reactor to operate on the stirrer. The coil was driven by a d.c. motor between limit switches. Filling of the reactor with the major ingredients, ethylene and propane, was accomplished successively by freezing these gases into the reactor under liquid nitrogen from a known volume between known pressures. The initiator, redistilled di-t-butyl peroxide (DTBP), was placed in the previously evacuated and ethylene flushed reactor inside a thin-walled glass ampule. The latter had been filled with thoroughly degassed DTBP on a vacuum line. The initiator was introduced into the ampule as a known volume from a hypodermic syringe, either pure or as 10% or 1% solutions in distilled thiophene-free benzene. The latter never exceeded 0.2 weight per cent. of the final mixture, and its presence had no effect on the kinetics of the reaction. The ampule was crushed as the gases began to develop pressure in warming and the mixture was stirred thoroughly before immersing the reactor in the oil-bath.

Use of ethylene and propane of very low oxygen content (never exceeding 2-5 p.p.m.) and careful exclusion of oxygen during filling is required in order to obtain reproducible kinetic data, especially at the higher pressures. At pressure exceeding about 1,700 atm. oxygen levels of 2 p.p.m. can give appreciable rates of polymerization,[8] but because of the autocatalytic nature of the oxidation step, ethylene containing very low oxygen levels can often be further purified by heating it for a period several times the induction period for polymerization, the gas then being entirely stable toward polymerization.[8] This procedure was followed in all runs above 1,300 atm. Polymerization took place only rarely during the pretreatment and, if so, only in trace amounts.

Materials.—The samples of ethylene (Monsanto Chemical Company) and propane (Matheson Company, Instrument Grade) had analyzed at less than 3 p.p.m. oxygen, and the ethylene, judging from its stability toward polymerization above 2,000 atm., probably contained only about 1 p.p.m. oxygen. DTBP stated to be 99% pure was obtained from the Shell Development Company and redistilled before use.

Calculation of Ethylene and Propane Concentrations.— The ethylene and propane concentrations in the reactor could be calculated from the filling pressures, the filling vessel[8] and reactor volumes and a knowledge of the compressibility factors. Accurate P, V, T data were available for ethylene[11] up to 2,500 atm. and for propane up to 700 atm.[12] but generalized compressibility factor[13] charts had to

be used for propane at the higher pressures. In most cases, the molarity of the ethylene–propane mixture calculated from the filling pressures agreed within better than 5% with that calculated from the P, V, T data valid at the reaction temperature, assuming the compressibility factor for the mixture to be the arithmetic mean of that for the components.[13] The deviations were due largely to fluctuations in room temperature during filling and failure of the filling vessel to reach ambient temperature. This small fluctuation is unimportant kinetically, but in order to be consistent, the molar concentrations of ethylene and propane in each run were calculated as follows: The molar concentrations of pure ethylene and propane were assumed to be those obtained from the initial reaction pressure at the reaction temperature, making use of the data of Michels and Geldermans for ethylene[11] and our own calibration for propane which checked at the low pressure end with the data of Reamer, Sage and Lacey[12] and with the generalized compressibility factor. The total molarity for the mixtures was then calculated from the filling pressures and compared with that obtained from the calibration for the pure gases assuming the compressibility factor for the mixture to be the arithmetic mean, using the molarities obtained from the filling pressures. If the two differed significantly, each molar concentration was corrected by a factor equal to the ratio of the total molarity of the mixture obtained in these two ways. The concentrations reported were those of the initial mixture, except in the ethylene–propane dilution series where the ethylene concentration at the time of the rate measurement is reported (see below). It was only in the latter case that the correction was significant.

Pressures vs. molarities for pure ethylene and for pure propane are plotted in Fig. 1. Where the molarity of only ethylene or propane is listed with the data, the other may be estimated quickly from Fig. 1 by the procedures described.

Calculation of Polymerization Rates.—Polymerization rates were obtained from the rate of pressure drop during reaction.[8] It was no longer permissible to assume equality of partial specific and specific volumes of the pure components as was done in the earlier study[8] because this assumption may be less justified in the present system and because of the greater accuracy required. A calibration of pressure drop vs. yield was therefore required over the pressure range under study (Fig. 2). The drop in yield per unit pressure drop with pressure reflects largely the decrease in compressibility of the monomer with pressure. This calibration curve parallels one calculated assuming no volume change of mixing polymer and solvent,[11,14] but lies below it. This indicates that the volume of mixing is negative and that the partial molar volume of the polymer is probably less than the molar volume. In performing the calibration, polymerizations were usually carried out to from 3 to 7 per cent. conversion, corresponding to pressure drops of roughly 150 to 300 atm. and no effect of conversion on the yield per unit pressure drop could be detected over this range. The abscissa of Fig. 2 corresponds to the average pressure of the calibration interval. Because of the moderate pressure coefficient of the polymerization rate this averaging procedure was adequate. All calibrations were performed at 20 to 50 mole per cent. propane where the polymer was always obtained as a solid. The same calibration curve was assumed to be applicable at the higher propane concentrations where the partly greasy product could not always be recovered quantitatively.

In determining polymerization rates, the average pressure drop per unit time was ordinarily determined over a pressure interval of about 50 to 100 atmospheres, starting at a pressure about 50 atmospheres below the initial pressure. This made it possible to avoid errors due to the slow temperature equilibration in the dead volume of the apparatus. In this way rates were nearly always determined at less than 5% conversion. In distinction to the oxygen-initiated polymerization,[8] induction periods and autoacceleration were absent and polymerization rates as a function of conversion were nearly steady, up to several per cent. conversion, moderated only slightly by the pressure coefficient of the polymerization rate.

Because of the relative incompressibility of the mixture, it was difficult to achieve exactly the desired initial pressure. Where data are reported at constant pressure (Fig. 3, 5),

(11) A. Michels and M. Geldermans, Physica, 9, 967 (1942).

(12) H. H. Reamer, B. H. Sage and N. W. Lacey, Ind. Eng. Chem., 41, 482 (1949).

(13) O. A. Hougen and K. M. Watson, "Chemical Process Principles II," John Wiley and Sons, New York, N. Y., 1947.

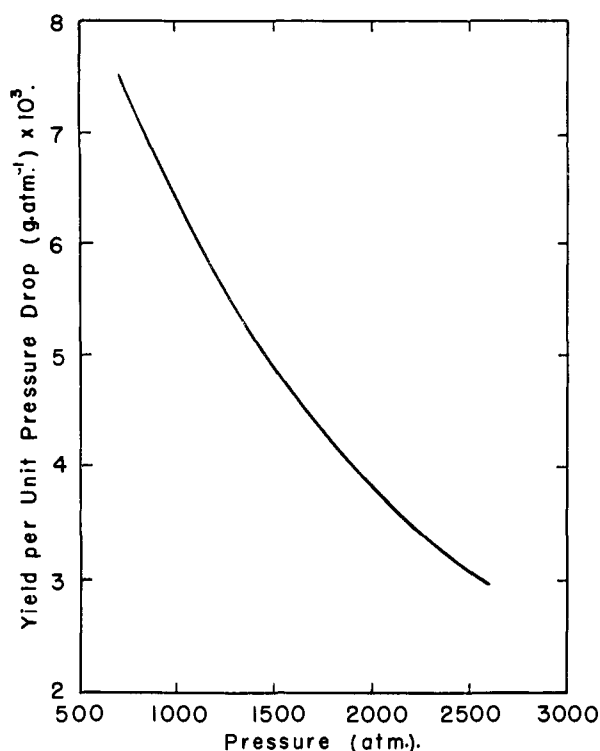(14) W. Parks and R. B. Richards, Trans. Faraday Soc., 45, 203 (1949).

Fig. 2.—Polymer yield per 1 atm. pressure drop vs. pressure.

Fig. 3.—Log polymerization rate vs. initiator concentration at 128.9° at a propane concentration of 4.0 moles $l.^{-1}$ and an ethylene concentration of 10.9, 13.4 and 15.9 moles $l.^{-1}$, respectively.

Fig. 4.—Log polymerization rate vs. pressure at 128.9° at a constant propane concentration of 3.8 moles $l.^{-1}$ ($\triangle$) and a constant ethylene concentration of 10.4 moles $l.^{-1}$(O). $[I] = 2.55 \times 10^{-3}$ moles $l.^{-1}$.

runs differing by about 10% in initial pressure are included and the pressure correction to the rate made is that established in the pressure variation study at constant initiator (Fig. 4). This correction was always less than 15%. Due to the more accurate recent calculations, there are some minor differences between the data reported here and those in the preliminary communication.[15]

Results

Figure 3 shows the effect of initiator concentration on the polymerization rate R_{pol} at several pressures and over a greater than 100-fold range in initiator concentration. In all cases, the rate increases with the initiator concentration to a power of between 0.5 and 0.6, indicating a close approach to bimolecular termination. Isothermal conditions could be maintained in the present equipment at steady rates approaching 5%/min. Under non-steady state conditions, rapidly decaying maximum rates several times greater could be tolerated in somewhat narrower reactors, with a very small or no temperature rise.[10] When operating at 900 atm. and in the absence of propane, the reaction order in initiator rises to values greater than 0.6 and becomes variable. Furthermore, thermal equilibrium can be upset at initial rates several times smaller than those tolerable in the presence of propane. These observations and other evidence[9] suggest very strongly that all experiments in the presence of propane were made under homogeneous conditions. Although the solvent action of propane is probably enhanced by its activity as chain transfer agent, it must be noted that propane is a better solvent than ethylene as measured on the identical polyethylene.[9]

(15) R. O. Symcox and P. Ehrlich, Polymer Division Abstracts, 139th Meeting of the American Chemical Society, St. Louis, Missouri, March. 1961.
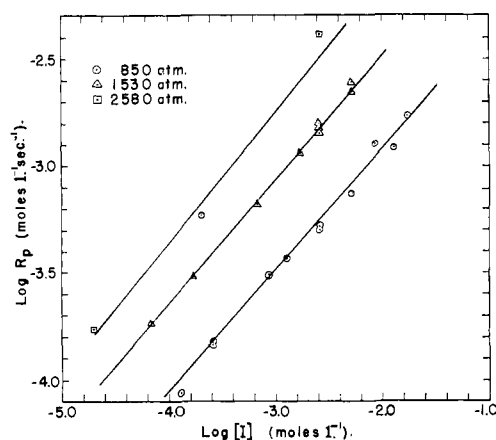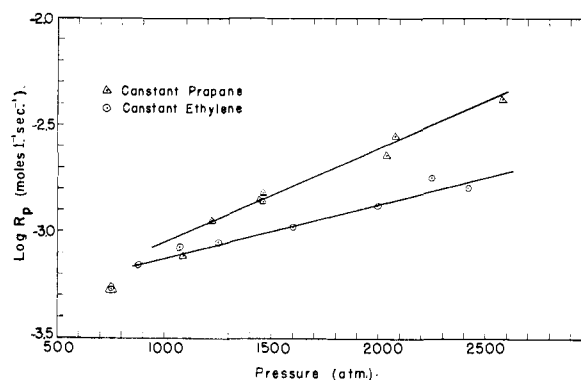
A plot of log R_{pol} vs. pressure is, within experimental error, linear both at constant propane and at constant ethylene concentration from 900 to 2,500 atm. (Fig. 4). The slopes are 4.4×10^{-4} $atm.^{-1}$ and 2.6×10^{-4} $atm.^{-1}$, respectively. The data suggest a substantial deviation from linearity below about 900 atm. As in the initiator study, isothermal rates at constant initiator could be maintained over a greater range of the variable studied than in previous work.[7,10] The pressure range overlaps with that of Laird, Morrell and Seed[7] at the low pressure end, but the present study shows a far smaller pressure coefficient of R_{pol}. Comparison of absolute rates is of little interest because of the different initiator dependencies.

The dependence of R_{pol} on the ethylene concentration at constant pressure is shown in Fig. 5. The log–log plots which are slightly curved indicate an apparent reaction order in monomer between one and two with the order increasing as the concentration of ethylene is lowered. Even at high propane concentrations, induction periods could not be observed and the deviation from first order kinetics can presumably not be accounted for by an impurity in the propane.
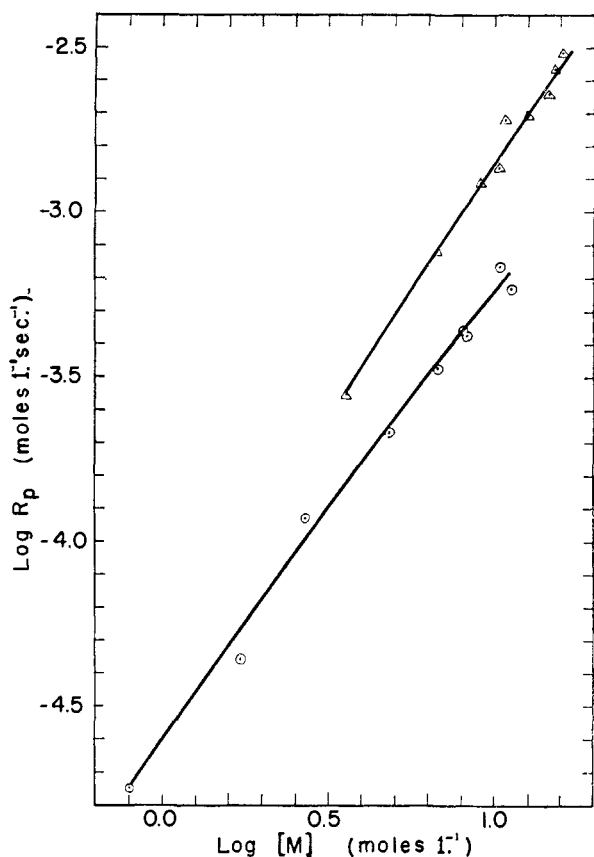
Fig. 5.—Log polymerization rate *vs.* log ethylene concentration at 128.9° and 885 atm. (O) and at 2,040 atm. (△). $[I] = 2.55 \times 10^{-3}$ moles $1.^{-1}$.

Discussion

Before interpreting the pressure and concentration coefficients of the polymerization rate, we discuss the application of the transition state theory to nonideal systems.[3,4] Since we are concerned primarily with the propagation step, we consider the reaction A + B→AB. According to the transition state theory, the rate constant k is proportional to the equilibrium ratio $c_{\pm}/c_A c_B$, where the c's are molar concentrations and the subscripts A, B and $\pm$ refer to species A, B and the activated complex, respectively. If k_0 is defined as being proportional to the true equilibrium constant, expressed in activities, the relation

$$k = k_0 \frac{\gamma_A \gamma_B}{\gamma_{\pm}} \qquad (1)$$

is obtained,[4] the standard states being as yet unspecified. Here the γ_i are the activity coefficients defined as the ratios of activity to *molar* concentration. In considering gaseous systems, the standard state chosen is usually that of the ideal gas at 1 atm. k_0^g is then independent of pressure and the pressure coefficient of k is given by the variation with pressure of the terms γ_i^g where the superscript g refers to the choice of the ideal gas at 1 atm. as standard state. An analysis of the pressure coefficient of the polymerization rate using this standard state was attempted by Laird, Morrell and Seed.[7]

It seems more useful to choose the standard state marked by superscript*, denoting the pure component at the pressure of the mixture. Since the rate constant must be independent of the standard state chosen, we have

$$k = k_0^g \frac{\gamma_A^g \gamma_B^g}{\gamma_{\pm}^g} = k_0^* \frac{\gamma_A^* \gamma_B^*}{\gamma_{\pm}^*} \qquad (2)$$

Expressed in terms of the standard state *, k is given by an equation identical with that used for liquid systems. The individual terms γ_i^* are defined by $(1/c_i) \cdot (f_i/f_i^*)$, f denoting fugacity, the summation being carried out as required by equation 2. The term $\sum_i \delta \ln \gamma_i^*/\delta P$ is usually small in liquids. According to the Lewis–Randall rule, $f_i = f_i^* N_i$, where the N_i refer to mole fractions; to the extent that it is valid, $\sum_i \delta \ln \gamma_i^*/\delta P$ is given only by differences in compressibility of reactants, diluent and complex, just as with liquids. One may therefore argue that, for highly compressed gases, this term should be of nearly equally small importance. The quantity k_0^g is by definition independent of pressure, whereas $\delta \ln k_0^*/\delta P$ is given by $-\Delta V_{\pm}/RT$ where $\Delta V_{\pm}$ is the molar volume of activation. We have then, to the extent that $\sum_i \delta \ln \gamma_i^*/\delta P$ can be ignored for the present gaseous (or, more properly, supercritical) system

$$\frac{\delta \ln k}{\delta P} = \sum_i \frac{\delta \ln \gamma_i^g}{\delta P} = -\frac{\Delta V_{\pm}}{RT} \qquad (3)$$

the differentiations being performed at constant temperature and mole fractions of all components. It follows that even in a gaseous system at high pressure the pressure coefficient of the rate constant may be visualized in terms of a volume of activation. The latter may be calculated from theory[4,6] or approximated by equating transition and final states, whereas this is not true in general for $\Sigma \delta \ln \gamma_i^g/\delta P$.[7]

There is much evidence from liquid phase polymerization that, provided the kinetics is not diffusion controlled, $\Delta V_{\pm}$ can be approximated to the volume change for propagation[5,16] and hence to the volume change of polymerization, ΔV_{pol}, since the properties of the transition state are supposed to be fairly close to those of the final state. It follows from Equation 3 that we should have for the over-all rate constant for polymerization k_{pol}

$$\frac{\delta \ln k_{pol}}{\delta P} \sim -\frac{\Delta V_{pol}}{RT} \qquad (4)$$

Laird, Morrell and Seed, using the transition state theory and having chosen the ideal gases as standard states arrive at the conclusion that the rate of polymerization R_{pol} should be proportional to the monomer fugacity.[7] This conclusion does not seem reasonable, since it requires that $\delta \ln R_{pol}/\delta P$ be given by $\bar{v}_M/RT$, where the subscript M refers to the monomer and $\bar{v}$ is the partial molar volume; it arises from what appears to be an arbitrary cancellation of all γ_i^g, except that of ethylene.

(16) F. M. Merrett and R. G. W. Norrish, *Proc. Roy. Soc. (London)* **A206**, 309 (1951).

Equation 3 assumes constancy of all mole fractions N_i. The variation of $\gamma_A{}^*\gamma_B{}^*/\gamma_\pm{}^*$ at constant pressure must therefore be examined to determine whether k changes with the concentration of ethylene at constant pressure and whether the identification of $\delta \ln k_{pol}/\delta P$ with $- \Delta V_{pol}/RT$ can be maintained as the mole fraction of ethylene changes at constant ethylene molarity. The total molarity does not vary greatly as the ethylene/propane ratio is changed and only the variation of $\gamma_M{}^*$ with composition at constant pressure need be considered. According to the Lewis–Randall rule, this term varies as N_M/c_M; it modifies slightly the identification of $\delta \ln k_{pol}/\delta P$ with $- \Delta V_{pol}/RT$ under the conditions of these experiments and predicts a reaction order in monomer slightly lower than one. The effects of a change in total molarity at constant pressure on the other two γ^* terms will be equally small individually and cancel.

It may be worth noting that, in terms of the transition state theory, any effects due to non-ideality are absorbed by the rate constant, as indicated by equation 1 and 2 and not by the concentration terms, preserving the usual relation between reaction rate, rate constant and concentration, i.e., the rate constant for a bimolecular reaction is still defined by $d(c_{AB})/dt = kc_Ac_B$.

In view of the kinetic analysis presented, the interpretation of the effect of initiator concentration on R_{pol} (Fig. 3) is straightforward and identical to that in liquid systems; it indicates a close approach to bimolecular termination and the absence of induced decomposition. There is no doubt that the initiator is completely soluble in the reacting gases. The solvent power of compressed non-polar gases for liquids and even solids of different internal pressure is usually far greater than that given by the Poynting effect because of a large interaction term.[17] The slope λ of Fig. 4 at constant ethylene should be interpretable in terms of $\Delta V_\pm$, and hence ΔV_{pol}. According to equation 3, $\Delta V = -2.303\lambda RT$ and equal to $- 20$ cc./mole. If we allow for the slightly decreasing mole fraction of ethylene by allowing $\gamma_M{}^*$ to change as N_M/c_M, $\Delta V_\pm$ becomes $- 23$ cc./mole.

In interpreting this value of $\Delta V_\pm$ in the light of equations 3 and 4, we first compute the average difference in molar volume per monomer unit of pure polymer and molar volume of monomer, $V_{pol} - V_M$, at 1,000 to 2,500 atm. This is $- 23$ cc./mole. The exact agreement with $\Delta V_\pm$ is probably fortuitous, since additional factors have to be considered. Two of these are the somewhat larger probable volume of the transition state compared to the final state and the probably smaller partial molar volume of the dissolved polymer compared to its molar volume, as suggested by the calibration. These two effects will act in opposite directions and tend to cancel. In addition, equation 4 assumes that the sum of the contributions to $\Delta V_\pm$ of the initiation and termination steps are unimportant.[18] The former is probably small (see below), whereas it is more difficult to

assess the importance of the latter. It, too, should be small, however, for a fast bimolecular reaction which is not diffusion controlled,[4] and it is not of dominant importance even in systems such as styrene where diffusion controlled termination seems established.[5,19] In spite of these uncertainties, one would therefore expect equation 4 to provide an approximate representation of the data; the fact that it does would seem to provide considerable evidence in favor of the volume of activation theory. On the other hand, if the rate were proportional to the monomer fugacity, $2.303\lambda RT$ would be given by $(\delta \ln f_M/\delta P)RT$ or $\bar{V}_M$ which, at low conversions, should be given closely by V_M. The latter term averages about 52 cc./mole rather than the experimental 20 to 23 cc./mole. This appears to invalidate the analysis based on monomer fugacities.[20]

Caution seems advisable in advancing a reason for the failure of the reaction to follow first order kinetics in monomer, a phenomenon not uncommon in free radical polymerization kinetics. A possible reason may be the smaller reactivity of secondary and tertiary radicals formed with increasing frequency upon adding propane. The explanation may, however, be connected with the somewhat uncertain conversion of activities to concentrations inherent in the use of the transition state theory.

Values of the parameter $R_{pol} [M]^{-1}\{k_d[I]\}^{-1/2}$ obtained from the data of Fig. 4 are listed as a function of pressure in Table I, where M and I refer to monomer and initiator and k_d is the decomposition rate constant of the latter.

TABLE I

THE PARAMETER $R_{pol}[M^{-1}]\{k_d[I]\}^{-1/2}$ AT 129°

Pressure (atm.)	$R_{pol}[M]^{-1}\{k_d[I]\}^{-1/2}$ (l.$^{1/2}$ mole$^{-1/2}$ sec.$^{-1/2}$)
750	0.22
1000	.30
1500	.40
2000	.54
2500	.73

If the usual steady state law for vinyl polymerization applies here, this parameter is equal to $k_p(\epsilon/k_t)^{1/2}$ where k_p and k_t are the rate constants for propagation and termination and ϵ the initiator efficiency. In these calculations k_d was assumed to equal 2.2×10^{-5} sec.$^{-1}$.[21] The deviation from first order monomer dependence might seem to call the validity of the relation somewhat into question, but the data of Table I correspond to high mole fractions in ethylene and the error in extrapolating to pure monomer should not be large. The values listed should therefore correspond closely

(17) J. S. Rowlinson and M. J. Richardson in Advances in Chemical Physics," Vol. II, Interscience Publishing Co., New York, N. Y., 1959.

(18) If not, equation 38 of ref. 5 must be used. Diffusion control of the termination step would therefore increase the pressure coefficient of the over-all rate constant.

(19) A. E. Nicholson and R. G. W. Norrish. Discussions Faraday Soc., 22, 104 (1956).

(20) A similar conclusion has recently been reached, based on work on the γ-ray initiated polymerization of ethylene at lower pressures (R. H. Wiley, N. T. Lipscomb, F. J. Johnson, G. A. Akin and J. E. Guillet, Paper C20, presented at IUPAC International Symposium on Macromolecular Chemistry, Montreal, July 29, 1961).

(21) J. H. Raley, F. F. Rust and W. E. Vaughan, J. Am. Chem. Soc., 70, 1336 (1948); F. Lossing and A. W. Tickner, J. Chem. Phys., 20, 907 (1952).

to pure ethylene polymerizing under hypothetical homogeneous conditions. The calculation also assumes that k_d is independent of pressure. The rate constants of unimolecular decomposition often decrease somewhat with pressure,[6] but the pressure coefficient of k_d for DTBP varies with the solvent,[22] and it seems hazardous to assume a particular correction factor valid for the present case. Experiments in which it was attempted to measure rates of initiation with diphenyl picryl hydrazyl gave unsharp induction periods but suggested that the initiation rate decreased by less than 30 per cent. as the pressure was increased over the interval considered in Table I. We conclude that the values of $R_p[\mathrm{M}]^{-1}\{K_d[\mathrm{I}]\}^{-1/2}$ listed provide a good approximation to the value of k_p-$(\epsilon/k_t)^{1/2}$ and its pressure coefficient. Assuming the efficiency factor ϵ to be of the order of unity, it is of interest to compare the values of Table I with those obtained at lower pressures. Values of $k_p/k_t^{1/2}$ reported for low pressure systems at $130°$ vary from 0.03 to 0.3 $1.^{1/2}\,\mathrm{mole}^{-1/2}\,\mathrm{sec.}^{-1/2}$,[23] whereas

(22) C. Walling and G. Metzger, J. Am. Chem. Soc., 81, 5365 (1959).

(23) A. L. Mandelcorn and E. W. R. Steacie, Can. J. Chem., 32,

an intermediate pressure system (less than 100 atm.) at $83°$ gave a value of 0.015^{24} which, assuming $E_p - E_t/2$ (the activation energies for propagation and termination) to equal 7 kcal. would give 0.05 at $130°$. Clearly, these values are on the average lower, but within about an order of magnitude of those reported here, and the difference is probably accounted for by the large pressure gap existing between them. Laita[24] has measured k_p and k_t separately and attributed the reason for the surprisingly low value of $k_p/k_t^{1/2}$ for ethylene, both, to the high termination constant of 10^9 and a rather low propagation constant.

474 (1954); J. A. Pinder and P. J. LeRoy, ibid., 35, 588 (1957); D. W. Lampe and F. H. Field, ibid., 37, 995 (1959); L. C. Landers and D. H. Volman, J. Am. Chem. Soc., 79, 2996 (1957); R. K. Brinton, J. Chem. Phys., 29, 781 (1959); J. A. Kerr and A. F. Trotman-Dickenson, Trans. Faraday Soc., 55, 572 (1959).

(24) Z. Laita, J. Polymer Sci., 38, 247 (1959); Z. Laita and Z. Machacek, ibid., 38, 459 (1959).

Thermodynamic Properties of Donor–Acceptor Complexes

BY WILLIS B. PERSON[1]

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The empirically observed linear relations between ΔS and ΔH for series of different donors with a standard acceptor are examined. Investigation of the various terms contributing to ΔH and ΔS suggests that the linear relations are due to a linear relation between ΔS_v and ΔE_0^0. The latter relation can occur if the logarithms of the new force constants in the complex are linearly proportional to ΔE_0^0. Empirical examination of this relation suggests it is probably reasonable for a series of chemically related donors with a standard acceptor.

Introduction

One of the characteristics of the thermodynamic properties of electron donor–acceptor complexes is that the entropies of formation of a set of complexes depend linearly on the enthalpy changes when these properties are compared for a series of related donors with a standard acceptor molecule. Such linear relations have been noted particularly for hydrogen bonded complexes[2] and for complexes in which iodine is the acceptor.[3-6] A qualitative explanation for this relationship is that the decrease in entropy on forming the complex becomes greater due to the more restricted configuration of the atoms as the complex becomes more stable (ΔH becomes a larger negative quantity). However, it is not obvious that the relationship between ΔS and ΔH should be *linear*, nor is it clear just which of the various con-

(1) Guggenheim Fellow, 1960–1961. On leave of absence from the University of Iowa, Iowa City, Iowa.

(2) G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond," W. H. Freeman and Co., San Francisco, Calif., 1960.

(3) L. S. Andrews and R. M. Keefer. J. Am. Chem. Soc., 77, 2164 (1955).

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tributions to ΔS and ΔH should be most important in determining the relationship between them. In order to gain some insight into these questions, let us briefly review the calculation of ΔH and ΔS for a typical donor–acceptor reaction.

Calculation of ΔH and ΔS

Consider the gas-phase reaction

$$\mathrm{NH_3 + I_2 = NH_3 \cdot I_2}$$
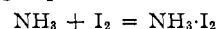
The procedure for calculating ΔH and ΔS for such a reaction is very well known. Shepp and Bauer,[7] for example, give details of such calculations for similar reactions. The calculations for the ammonia–iodine reaction are summarized in Table I. We see there that ΔS is the resultant sum of a large negative term, ΔS_{tr+r}, due mostly to the loss of five translational and rotational degrees of freedom by the system, and a smaller positive terms, ΔS_v, due to the five new vibrational degrees of freedom of the complex.

In Table I, we see that the value of ΔS_{tr+r} is essentially independent of the donor. Varying the donor will change slightly the values of the mass ratio and the ratio of moments of inertia, but the dominant term in ΔS_{tr+r} is the term containing the

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