tetramethylene biradicals which have been assumed to be intermediates in the photolysis of cyclopentanone.[5,6] The formation of butene and ethylene from the tetramethylene biradical has been observed by Bawn and Milsted[30] in their study of the reaction of 1,4-dibromobutane and sodium at 300°.

In spite of the data which are available the complexity of the cyclopentanone decomposition precludes a thorough consideration of the detailed mechanism at the present time.

Acknowledgment.—The authors wish to thank Mr. Carl Whiteman for making the infrared measurements and Dr. F. L. Mohler of the National Bureau of Standards for the mass spectrometric analyses.

ROCHESTER, N. Y.

[30] C. E. H. Bawn and J. Milsted, *Trans. Faraday Soc.*, **35**, 889 (1939).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF ROCHESTER]

The Thermal Decomposition of Cyclobutanone[1]

BY M. N. DAS, F. KERN, T. D. COYLE AND W. D. WALTERS

RECEIVED JULY 15, 1954

The homogeneous thermal decomposition of cyclobutanone has been investigated over the temperature range 333–373°. The decomposition proceeds essentially by a reaction forming ethylene and ketene as the primary molecular products. For experiments conducted at initial pressures from 10 to 88 mm. at 368° first-order kinetics were observed. The change in rate constant with temperature is given by the relationship $k = 3.6 \times 10^{14} e^{-52000/RT}$ sec.$^{-1}$. The decomposition is not inhibited by the addition of propylene, toluene or nitric oxide.

In view of the apparent simplicity of the homogeneous thermal decomposition of cyclobutane[2] which forms two molecules of ethylene by a nonchain process, it was of interest to investigate the products and kinetics of the thermal decomposition of cyclobutanone as another example of a compound having a four-membered ring structure. The photochemical decomposition of cyclobutanone has been investigated already.[3,4] Benson and Kistiakowsky[3] found that ethylene and ketene, as well as propylene and carbon monoxide, are formed by the ultraviolet irradiation of cyclobutanone, indicating that at least two reaction paths are possible photochemically. The analytical results did not permit a decision concerning the presence or absence of cyclopropane. Recently Blacet and Miller[4] have observed that cyclopropane predominates over propylene in the photolysis at 3130 Å. but is approximately equal to propylene at 2654 Å.

Experimental

Materials and Apparatus.—Cyclobutanone from two different sources was used in the present work. Sample A which was a purified sample prepared by the method of Roberts and Sauer[5] was generously furnished by Dr. F. E. Blacet. Measurement of the index of refraction gave values in the range 1.4198–1.4182 for temperatures 25.1–26.0° in comparison with a reported value[5] of n^{25}D 1.4189. This sample was used without further treatment except that drying over anhydrous calcium sulfate or separation into several fractions by trap to trap distillation under vacuum was performed on the material before certain experiments. Sample B which was supplied by the Chemicals Procurement Company was purified by preparation of the semicarbazone; the regenerated ketone was fractionated in a spinning band column. The various fractions of the samples are designated by I, II, etc. Infrared absorption curves were obtained for samples AI, BII, BIII and BIV; they agreed well with each other and with a published curve[5] except for the possible presence of a trace of water in BII. In some of the experiments BII was dried before use, but no significant difference in rate was observed. In order to carry out a different type of purification several fractions from each of the samples above were combined and converted into the bisulfite derivative. The material regenerated from the bisulfite derivative will be referred to as sample C. Vapor pressures[6] of several portions were measured and compared with the values calculated from Benson and Kistiakowsky's equation.[3]

Propylene (99.5%) was obtained from the Ohio Chemical and Manufacturing Company and was subjected to repeated degassing at −196°. Nitric oxide (98%) supplied by the Matheson Company was purified by two distillations from −160 to −196°. Analyzed reagent grade toluene was dried over anhydrous calcium sulfate. All materials were thoroughly degassed just before introduction into the reaction vessel.

The early experiments were performed in a 360-ml. Pyrex reaction bulb with a thermocouple well at its center. Temperatures were measured with a platinum, platinum–13% rhodium thermocouple attached to a Leeds and Northrup Type K-2 potentiometer. The mercury manometer (3 mm. bore) was heated electrically to prevent the condensation of cyclobutanone. In some experiments a reaction vessel packed with thin-walled Pyrex tubes was used; this bulb provided a 17-fold increase in the surface to volume ratio. Most of the experiments were carried out in a second apparatus with an unpacked cylindrical Pyrex vessel of 500-ml. capacity. The furnace and apparatus for temperature control were a modification of a type previously used.[7] The temperature was measured with another platinum, platinum–13% rhodium thermocouple connected either to the Type K-2 potentiometer or to a Gray Model E-3040 potentiometer. The thermocouple was standardized at the melting point of zinc. Pressures below 17 mm. were measured with a 20 mm. bore mercury manometer read with a cathetometer. Pressures above 17 mm. were measured with a 6 mm. bore mercury manometer which was heated when necessary to avoid condensation.

In a series of experiments at 368° the rate of decomposition in the packed bulb with a 17-fold greater surface to volume

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[1] This work has been supported by a grant from the Celanese Corporation of America.

[2] C. T. Genaux and W. D. Walters, THIS JOURNAL, **73**, 4497 (1951); C. T. Genaux, F. Kern and W. D. Walters, *ibid.*, **75**, 6196 (1953).

[3] S. W. Benson and G. B. Kistiakowsky, *ibid.*, **64**, 80 (1942).

[4] F. E. Blacet and A. Miller, Abstracts, A. C. S. Meeting, Chicago, Illinois, September 6–11, 1953, p. 18R.

[5] J. D. Roberts and C. W. Sauer, THIS JOURNAL, **71**, 3925 (1949).

[6] The following list gives the sample designation followed by the temperature, the observed vapor pressure in mm., and the calculated value in parentheses. A: 0°, 10.9 (10.3); 23.2°, 38.8 (38.7). BII: 0.2°, 11.0 (10.5); 22.8°, 40.2 (37.9). BIII: 0.2°, 10.4 (10.5); 22.9°, 37.1 (38.1); 23.8°, 39.7 (40.0). C: 0.2°, 11.2 (10.5).

[7] D. W. Vanas and W. D. Walters, THIS JOURNAL, **70**, 4035 (1948).

ratio was compared with the rate in the unpacked bulb. The time for 25% pressure increase in three experiments in the packed vessel at pressures from 26 to 32 mm. averaged only 7% longer than the mean of four experiments in the unpacked vessel at 29–35 mm. In view of the large increase in surface produced by the packing it appears that there will not be a significant effect of the surface in the unpacked vessel in the early stages of the decomposition. It is to be noted that these findings apply to reaction vessels which have been deactivated or poisoned by use. That increased surface may affect the subsequent behavior of the primary products is indicated by the fact that for 30 mm. of cyclobutanone at 368° the maximum pressure attained in the packed vessel was about 87% of that in the unpacked vessel. In order to minimize any effect of the surface, particularly upon the secondary reactions, the initial experiments which were performed in a newly installed reaction vessel or after exposure to air and the first experiment on any day after several days without use were usually regarded as "poisoning" experiments and not employed for kinetic purposes.

The infrared absorption curves of the volatile reaction products from each of the three samples showed that ketene and ethylene are the principal gaseous products in the early stages of the decomposition. For a quantitative, as well as a qualitative, determination of ketene the reaction products were brought into contact with water and the acetic acid formed was titrated with standard sodium hydroxide. Precautions were taken to avoid errors likely to be caused by the presence of carbon dioxide. The amount of ethylene produced in the reaction was measured by its absorption in activated sulfuric acid.[8] Prior to the analysis for ethylene the products volatile at −78° were treated with aniline or acetic acid to remove ketene. A mass spectrometric analysis performed by the Consolidated Engineering Corporation confirmed the importance of ethylene in the gaseous products non-volatile at −196° and volatile at −78° from which ketene had been removed by chemical treatment; the analysis obtained for an experiment with 24 mm. cyclobutanone carried to 33% pressure increase at 368° was: ethylene, 99.4%; cyclopropane, 0.5%; carbon dioxide 0.1%. In the first two experiments which will be shown later in Table II, at least 98% of the −78° fraction (after removal of ketene) was absorbed in activated sulfuric acid. The amounts of the gases non-condensable at −196° observed in the experiments in Tables I and II were ordinarily very small, *i.e.*, ~ 1% of the quantities of gas volatile at −78°.

Results

Stoichiometry.—The analytical data indicate that the homogeneous thermal decomposition of cyclobutanone occurs according to the equation

$$\begin{array}{l} CH_2{-}CH_2 \\ | \quad\;\;\; | \\ CH_2{-}CO \end{array} \longrightarrow \begin{array}{l} CH_2{=}CH_2 \\ \\ CH_2{=}CO \end{array}$$

On the basis of this reaction it would be expected that in a constant volume apparatus the pressure of ketene formed or the pressure of ethylene at a given time would equal the pressure increase. The results from the analyses for ketene (Table I) and for ethylene (Table II) show that this is essentially the case when neither the initial pressure nor the percentage of decomposition is large. The data in Tables I and II indicate that the reaction in the early stages at low pressures can be satisfactorily followed by pressure measurements. In several experiments the reaction was allowed to proceed until a final pressure or a maximum pressure was reached. With two low pressure experiments (5.57 and 10.25 mm. at 368°) the ratio of the final pressure to the initial pressure was found to be 1.95, but at initial pressures of 29 and 66 mm. the values of the ratio of maximum pressure to the initial pressure were 1.92 and 1.77 respectively. The results at the higher pressures gave evidence for the occurrence of a pressure-decreasing reaction, probably involving ketene, which takes place subsequent to the primary decomposition and eventually causes the pressure to decrease slowly from the maximum value. For this reason experimental conditions were chosen to avoid as far as possible the presence of larger ketene pressures.

TABLE I

KETENE FORMED DURING THE DECOMPOSITION OF CYCLOBUTANONE AT 368°

Sample	$P^\circ_{C_4H_6O}$, mm.	Press. increase, mm.	P_{ketene}, mm.
A	33.4	14.6	14.7
A	33.3	14.6	14.5
A	23.3	11.4	11.2
A	13.9	7.2	6.7
BIII	22.5	12.5	11.8
BIV	30.4	13.1	13.8

TABLE II

ETHYLENE FORMED DURING THE DECOMPOSITION OF CYCLOBUTANONE AT 368°

Sample	$P^\circ_{C_4H_6O}$, mm.	Press. increase, mm.	$P^a_{C_2H_4}$, mm.
AII	5.43	2.85	2.91[b,c]
BII	59.7	27.8	28.2[c]
BII	33.8	13.4	14.6[d]
BIII	24.0	8.0	7.2[e]

[a] For this analysis the gases non-volatile at −196° and volatile at −78° were used. [b] In one experiment (not shown) with recovered cyclobutanone of questionable purity the material absorbed in activated sulfuric acid amounted to 10.5% more than the expected quantity. [c] Absorbed in activated sulfuric acid. [d] Total volume of gas non-volatile at −196°, volatile at −78°. [e] Mass spectrometric analysis.

Kinetics.—Figure 1 shows a plot of the quarter-times for the decomposition of cyclobutanone at 368° (corrected for dead space) against the initial pressure. The constancy of the quarter-time over the pressure range 10—88 mm. is an indication of the first-order character of the decomposition. This is corroborated by the fact that a plot of log $(2P_0 - P_t)$ *versus* time is linear over about 75% of the decomposition for experiments with initial pressures of 4.5 and 10.3 mm. For pressures in the range 30—66 mm. a linear relationship exists until approximately half of the cyclobutanone has decomposed. With several experiments at an initial pressure near 15 mm. the values of $t_{1/2}/t_{1/4}$ averaged 2.43 in comparison with 2.41 for a first-order reaction.

In a series of experiments summarized in Table III cyclobutanone was decomposed in the presence of propylene, toluene or nitric oxide in order to ascertain whether the reaction could be inhibited. Within the experimental error no inhibition was observed. Table III also gives the results of experiments in which the cyclobutanone was subjected to various treatments as a test for any impurities which might be influencing the rate. The treatments resulted in no significant change in the rate as measured by the quarter-time. In Table III where an average value for the quarter-time is given the mean deviation is shown if it exceeds

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(8) H. Tropsch and W. J. Mattox, *Ind. Eng. Chem., Anal. Ed.*, **6**, 404 (1934).

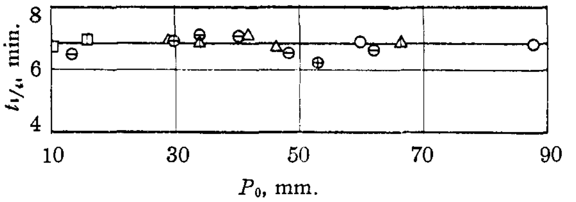

Fig. 1.—Values of the quarter-time at 368° for different initial pressures of cyclobutanone: 360-ml. vessel, sample A, △; 500-ml. vessel, sample A, □; sample BII, ○; sample BIII, ⊖. Vertical line through a point denotes that the point is the average of two or more experiments.

0.1 min. The deviation of the experiments, which frequently was greater than would be expected from the accuracy of the pressure and temperature measurements, may have been due in part to the effect of differences in surface conditions upon the secondary reactions of ketene.

TABLE III

DECOMPOSITION OF CYCLOBUTANONE AT 368°

Sample	Pressure, mm.	No. expts. av.	Treatment	$t_{1/4}$ min.
A	15.3	4	....	7.0 ± 0.3
A	15.6	2	6 mm. C_3H_6[a]	6.6
A	16.2	1	5.7 mm. C_7H_8[a]	6.7
A	15.9	3	0.04–0.15 mm. NO	6.8
A	15.7	1	0.35 mm. NO	6.9
A	15.4	1	Pre-pyrolysis[b]	6.8
A	14.8	1	$CaSO_4$[c]	6.7
BIII	29.5	4	....	7.0 ± 0.3
BIII	29.6	2	10 mm. C_3H_6[a]	6.7
BIII	31.8	4	10 mm. C_7H_8[a]	7.0 ± 0.3
BIII	28.7	1	$CuSO_4$[c]	7.3
BIII	31.4	1	$KHCO_3$[c]	7.0
A	10.3	1	....	6.7
BII	9.5	1	....	7.1
C	9.3	1	From bisulfite deriv.	6.9

[a] C_3H_6 and C_7H_8 mean propylene and toluene, respectively, present in the reaction bulb. [b] Cyclobutanone sample separated from a previous reaction mixture carried to 25% decomposition; products removed by pumping at −78°. [c] Cyclobutanone treated with solid before pyrolysis.

The activation energy for the decomposition was determined in experiments conducted at temperatures from 333 to 373°. The logarithms of the rate constant in sec.$^{-1}$ were plotted against the reciprocal of the absolute temperature as shown in Fig. 2. The rate constants were computed on the basis of a first-order equation from the values of $t_{1/4}$ taken from the pressure–time curve. In the determination of $t_{1/4}$ appropriate corrections were made for dead space. The points show the rate constants at 15 mm. for two samples and at 30 mm. for one sample. Since the data in Fig. 1 indicated that there is no change in rate constant over this pressure range, any differences in the locations of the points at a given temperature are caused chiefly by the experimental deviations. From the slope of the line the activation energy calculated to the nearest kcal. is 52 kcal./mole. The rate constant (on the basis of the 15–30 mm. experiments) can be expressed as: $k = 3.6 \times 10^{14} e^{-52000/RT}$ sec.$^{-1}$.

For a temperature of 368° at which most of the experiments were conducted this frequency factor when equated to $\kappa e(kT/h)e^{\Delta S\ddagger/R}$ gives a value of $\Delta S\ddagger$ equal to +4.6 cal./deg. mole. In this calculation the transmission coefficient κ has been assumed to be one. That the formation of the activated complex involves an increase in entropy would be anticipated for a ring cleavage reaction.

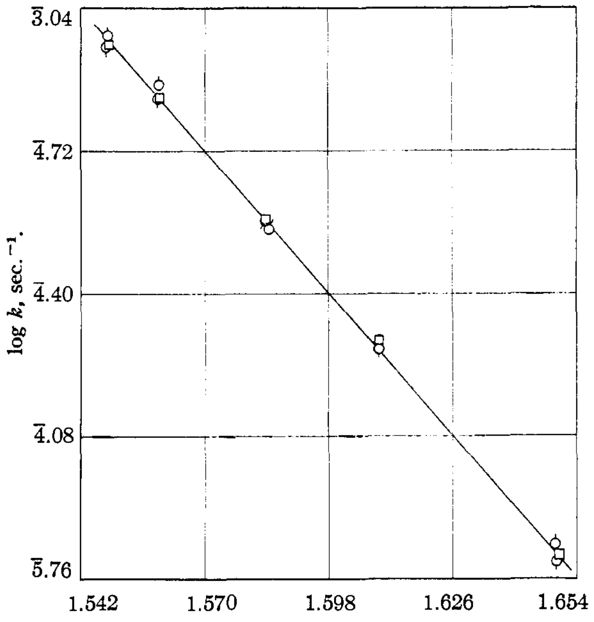

Fig. 2.—Change in rate with temperature: sample A, 15 mm., □; sample BIII, ~15 mm., ϕ; sample BIII, ~30 mm., ♀. The following points are averages of two or more experiments: sample A, all points; sample BIII, 30 mm., 373°, 368°, 358°; sample BIII, 15 mm., 373°.

Discussion.—The thermal decomposition of cyclobutanone seems to be a simple reaction both from the viewpoint of the products formed and from the kinetics. The occurrence of essentially a single reaction (forming initially ethylene and ketene with only traces of other products) is in contrast to the photochemical results obtained at lower temperatures.[3,4] The failure of propylene, toluene or nitric oxide to decrease the rate of the reaction gives evidence that the decomposition is not a free radical chain process. The possibility that biradicals may be present momentarily as intermediates in the decomposition cannot be excluded. The trace of cyclopropane which has been reported in a mass spectrometric analysis might be taken as an indication that biradicals exist during the thermal decomposition as in the case of the photolytic reaction.[4] On the other hand, definite evidence for the presence of cyclopropane[9] has not been obtained yet from the infrared observations. In view of the difficulty of analyzing for such a small amount of material and distinguishing it from traces of other substances, such as unremoved ketene or the pyrolytic products from ketene, it does not appear that a definite decision concerning the presence of cyclopropane can be made without further work.

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(9) In the infrared curves from some experiments there was an indication that a trace of propylene may be present.

The possibility of investigating the change in the rate constant at lower pressures has been considered and some experiments have been performed in the 4–10 mm. range. However, since the reproducibility of the experiments seems to become worse at the lower pressures, presumably as a result of more interference from heterogeneous processes, a detailed study of the rate at low pressures in the present apparatus did not appear to be worthwhile.

Acknowledgment.—The authors wish to thank Mr. Carl Whiteman for making the infrared absorption measurements.

ROCHESTER, NEW YORK

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE ROHM & HAAS CO.]

Inhibition of Polymerization. I. Methyl Methacrylate*

BY JOHN L. KICE

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The effect of nine compounds on the 2,2′-azo-bis-isobutyronitrile-catalyzed polymerization of methyl methacrylate has been studied kinetically by a dilatometric method. Where possible the data have been analyzed using a new equation, derived from a reasonable kinetic scheme, which permits a quantitative evaluation of the extent to which wastage of inhibitor takes place through "copolymerization." The results for benzoquinone and chloranil show that copolymerization is small for the former but almost 80% of the chloranil molecules disappear in this fashion without terminating kinetic chains. The rate constants obtained for the aromatic nitro compounds are compared with those previously reported for vinyl acetate and are found to be 10^5 smaller in methyl methacrylate. In addition it is found that even the stable free radical, 2,2-diphenyl-1-picrylhydrazyl, does not totally suppress the polymerization of methyl methacrylate during the induction period.

Introduction

Most of the quantitative information in the literature regarding inhibition of polymerization has been obtained with styrene and vinyl acetate. Thus Bartlett and Kwart[1] conducted a careful investigation of the effect of eleven compounds on the benzoyl peroxide-catalyzed polymerization of vinyl acetate, and a number of workers[2–4] have studied the action of various substances on the polymerization of styrene, both catalyzed and thermal. However, no extensive investigation of the behavior of inhibitors in methyl methacrylate polymerization has been reported, although Melville and co-workers[5,6] have studied the effect of quinone. The present investigation has been an attempt to partially rectify this situation.

To this end, the effect of nine inhibitors of various chemical types on the 2,2′-azo-bis-isobutyronitrile (AIBN) catalyzed polymerization of methyl methacrylate has been investigated using a dilatometric technique similar to that employed by Bartlett and Kwart.[1] All experiments were carried out at 44.1° in order to afford easy comparison with the data previously obtained at 45° with vinyl acetate.[1]

Experimental

Purification of Materials. Methyl Methacrylate.—Commercial monomer (Rohm and Haas) was washed repeatedly with 5% sodium hydroxide; it was then washed with water, followed by two washings with a saturated solution of sodium bisulfite in water. It was then washed twice more with water, dried over either Drierite or sodium sulfate and was then fractionally distilled under nitrogen at reduced pressure, only the middle cut being retained, b.p. 43° (90 mm.). After purification the monomer samples were stored in the dark at −20° in a desiccator until used. Freshly purified monomer was thus prepared every few weeks, and in addition the uninhibited polymerization rate of each batch of monomer was checked periodically during this period. In all cases these agreed with each other within the experimental error.

2,2′-Azo-bis-isobutyronitrile.—This was recrystallized from methanol until it showed a melting point of 103° dec. It was then stored at −20° under desiccation.

2,2-Diphenyl-1-picrylhydrazyl.—Material which had been prepared by the method of Goldschmidt and Renn[7] was recrystallized twice from chloroform–ether.

Benzoquinone.—This was recrystallized once from Esso octane, sublimed twice and then recrystallized again from octane, m.p. 114–115° (sealed tube).

Furfurylidene Malononitrile.—A sample was kindly supplied by Dr. R. N. Haward of Petrochemicals, Ltd. It was used as received.

Benzhydrilidene Malononitrile.—This was prepared according to the method of Schenk, *et al.*[8] Recrystallized twice from ethanol it melted at 138–139°.

Trinitrotoluene.—This was recrystallized once from methanol, m.p. 81–82°.

***m*-Dinitrobenzene.**—This was recrystallized from methanol, m.p. 89–90°.

***p*-Nitrotoluene.**—This was recrystallized once from methanol water, m.p. 50–51°.

Sulfur.—Reagent grade sulfur was recrystallized once from toluene.

Diphenylamine.—Eastman Kodak white label diphenylamine was recrystallized once from Esso octane, m.p. 50.5–51.0°.

The Dilatometer.—The dilatometers were similar in design to those employed by Bartlett and Kwart.[1] They were calibrated with mercury in the usual fashion to known marks in each capillary. From the density data of Fox and Loshaek[9] for monomer and polymer in monomer the volume change for complete polymerization at 44.1° was calculated to be 24.22%. From this and the volumes and capillary radii of the three dilatometers it was possible to ascertain the percentage polymerization for an over-all fall of 1 cm. in the capillaries. This was found to be 0.134, 0.138 and 0.142% for dilatometers 1, 2 and 3, respectively.

The procedure for a run was as follows. The proper amounts of initiator and inhibitor were weighed into a glass stoppered flask; a weighed amount of cold methyl methacrylate was quickly added, and solution was effected. About

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* Presented in part before the Division of Polymer Chemistry at the 126th Meeting of the American Chemical Society, New York, September, 1954.

[1] P. D. Bartlett and H. Kwart, THIS JOURNAL, **72**, 1051 (1950); **74**, 3969 (1952).

[2] G. V. Schulz, *Makrom. Chem.*, **1**, 94 (1947).

[3] F. A. Bovey and I. M. Kolthoff, *Chem. Revs.*, **42**, 491 (1948).

[4] J. W. Brietenbach and H. L. Brietenbach, *Ber.*, **75**, 505 (1942).

[5] H. W. Melville and W. F. Watson, *Trans. Faraday Soc.*, **44**, 886 (1948).

[6] E. Bonsall, L. Valentine and H. W. Melville, *ibid.*, **49**, 686 (1953).

[7] S. Goldschmidt and K. Renn, *Ber.*, **55**, 628 (1922).

[8] R. Schenk and H. Finken, *Ann.*, **462**, 267 (1928).

[9] T. G Fox and S. Loshaek, *J. Polymer Science*, in press.