Iowa State University

From the SelectedWorks of Steve W. Martin

December, 1986

On the glass transition and viscosity of phosphorus pentoxide

C. A. Angell, *Purdue University*
Steve W. Martin, *Purdue University*

Available at: https://works.bepress.com/steve_martin/43/

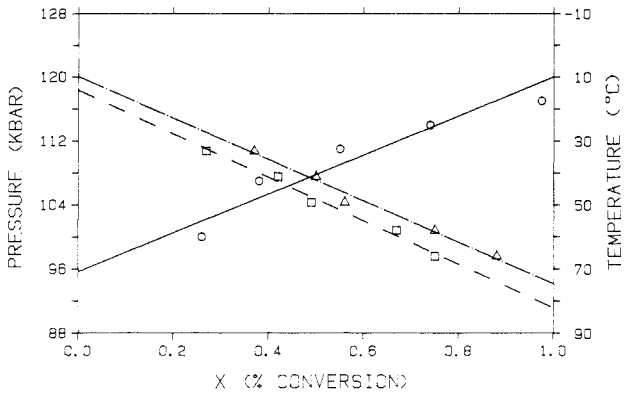

Figure 8. Plot of fractional conversion x after 50 h as a function of pressure and temperature: for pressure at 297 K (solid line) and for temperature at 10.7 (---) and 10.0 GPa (---).

walk" steps) which brings the p-DISN chains into configurations where the second step cycloadditions between adjacent p-DISN chains can procede.

Model calculations[16] indicate that, when the value of n is $^1/_2$, the mechanism involves a diffusion-controlled one-dimensional growth process; and empirical evidence suggests that the values of n for reactions controlled by diffusion are between 0.53 and 0.58.[17] These observations are not inconsistent with the first step in eq 5. The volume of activation for diffusion, however, should be positive; thus, a subsequent step with a large negative volume of activation must be rate-limiting. The cycloaddition in the second step of this mechanisms satisfies this requirement; typical volumes of activation for cycloadditions are -10 cm^3/mol.[18,19]

Another interesting observation can be made by extrapolating these data to lower pressures and temperatures. Figure 8 is a plot of the measured fractional conversion to paracyanogen after 50 h at several pressures and temperatures. On this time scale, polymerization is efficient above 10.7 GPa at 283 K, 10.0 GPa at 287 K, and 9.6 GPa at 293 K. This trend indicates that the pressure at which rapid polymerization begins decreases by about 1 GPa for every 30 K increase in temperature. Extrapolation of this trend to atmospheric pressure suggests that the pyrolytic synthesis of paracyanogen that is reported to occur above 620 K at low pressures follows the same mechanism.

Summary

The kinetics of formation paracyanogen from p-DISN have been measured between 290 and 350 K at 10 to 12 GPa by monitoring the growth of the $-C{=}N^-$ absorption bands between 900 and 1900 cm^{-1}. The experimental data can be explained by Avrami rate law with an exponent of 0.5 and rate constant of 0.057 h$^{-1/2}$ at 297 K and 10.0 GPa. The activation volume and enthalpy are -3.30 cm^3/mol and 28 kJ/mol, respectively. A two-step mechanism is suggested that involves diffusion of the p-DISN chains into an arrangement in which 4 + 2 cycloadditions occur between adjacent p-DISN chains.

Acknowledgment. Support provided for this work by grants from the U.S. National Science Foundation (DMR83-18812) and Los Alamos Branch of the University of California Institute of Geophysics and Planetary Physics (No. 028) are gratefully appreciated.

Registry No. Paracyanogen, 25215-76-3; poly(2,3-diiminosuccinonitrile) (SRU), 104619-15-0.

(16) Hulbert, S. F. *J. Br. Ceram. Soc.* **1969**, *6*, 11.
(17) Brown, W. E.; Dollimore, D.; Galwey, A. K. In *Comprehensive Chemical Kinetics*, Bamford, C. H.; Tipper, C. F. H., Eds.; Elsevier: New York, 1980; Vol. 22, p 71.
(18) Jenner, G. *Angew Chem., Int. Edit. Engl.* **1975**, *14*, 137.
(19) Van der Meer, R.; German, A. L.; Heikens, D. *J. Polym. Sci.* **1977**, *15*, 1765.

On the Glass Transition and Viscosity of P_2O_5

S. W. Martin† and C. A. Angell*

Department of Chemistry, Purdue University, West Lafayette, Indiana 47907 *(Received: May 19, 1986)*

The calorimetric glass transition temperature T_g for pure anhydrous P_2O_5 melted in sealed SiO_2 ampules at 1000 °C has been obtained directly for the first time with differential scanning calorimetry, and the increase in heat capacity at T_g has been determined. T_g measured in this way is 57 K higher than the value quoted in the literature, which is probably based on an Arrhenius law extrapolation of viscosity data to $\eta = 10^{13}$ P. Combining the high-temperature viscosity data with the common observation that, for oxide glasses, $\eta = 10^{12}$ P at the DSC T_g, we find that the P_2O_5 viscosity obeys an Arrhenius law over at least 6 decades of η. Furthermore, the intercept at $1/T = 0$ coincides with the common point of T_g-reduced viscosity plots for a wide variety of liquids recently used in establishing the "strong" vs. "fragile" classification of glass-forming liquids. On this basis, P_2O_5 behaves as the archetypal "strong" liquid. However, the value of C_p(liquid)/C_p(glass) at T_g, 1.27, is larger than expected on this basis since other "strong" liquids show smaller values, e.g., GeO_2 (1.09) and BeF_2 (no ΔC_p detected). The dependence of T_g on heating rate has been determined and shows that enthalpy relaxation in the transition region has, within error, the same activation energy (43.9 kcal/mol) as for viscous flow.

Introduction

In the course of studying the glass-forming characteristics of the binary system Li_2O–P_2O_5[1] we became aware that no well-defined measurement of the glass transition temperature of P_2O_5 has ever been recorded in the literature, although it is one of the three primary "glass formers." The value that is quoted,[2] T_g = 262 °C, is apparently based on the Arrhenius law extrapolation of viscosity data reported by Cormia et al.[3] in the temperature range 545–645 °C. A comparable value has been reported by Ray,[2b] but no details of the determination were given.

Over the limited temperature range of their study Cormia et al.[3] found the viscosity obeyed the Arrhenius law with the pa-

† Sohio Research Fellow, January 1984–January 1985. Present Address: Department of Materials Science & Engineering, Iowa State University, Ames, Iowa 50011.

(1) (a) Martin, S. W.; Angell, C. A. *J. Non-Cryst. Solids* **1986**, *83*, 185. (b) Martin, S. W.; Angell, C. A., to be published.
(2) (a) Sakka, S.; McKenzie, J. D. *J. Non*-Cryst. Solids **1971**, *6*, 145. (b) Ray, N. H. *J. Non*-Cryst. *Solids* **1974**, *15*, 423.
(3) Cormia, R. L.; Mackenzie, J. D.; Turnbull, D. J. *J. Appl.* Phys. **1963**, *34*(4), 2245.

0022-3654/86/2090-6736$01.50/0 © 1986 American Chemical Society

rameters in eq 1. Adopting the traditional idea that the viscosity of a liquid at its glass transition is 10^{13} P,[4,5] one can calculate T_g

$$\eta\ (\mathrm{P}) = 1.32 \times 10^{-4} \exp\left[\frac{41.5\ \mathrm{kcal\ mol^{-1}}}{RT}\right] \quad (1)$$

directly by using eq 1. One finds T_g to be 264.2 °C, close to the quoted values.[2] The assumption of Arrhenius behavior throughout the entire temperature range (and over ≈7 orders of magnitude in the viscosity) is a potential weakness of this estimate since very few liquids exhibit such behavior. If correct, it would imply that P_2O_5 is an unusually strong network liquid, in which case correlations of transport and liquid thermodynamic properties suggest[5-7] that it would provide a further example of a liquid with very small ΔC_p at T_g.

In order both to check the latter possibility and to provide a direct determination of T_g, we have performed differential scanning calorimetry heat capacity and heating rate studies on "anhydrous" P_2O_5 glass samples and report the results herein.

Experimental Section

Anhydrous P_2O_5 from the same manufacturer and of the same purity used by Cormia et al.[3] (Mallinckrodt, 98%) was placed into a flame-dried SiO_2 tube in the anhydrous environment of a high-quality drybox described previously.[8] The tube was evacuated at room temperature to ~25 μmHg over a liquid N_2 trap and sealed off with a gas torch. The sample was fused at 1000 ± 25 °C for 24 h to ensure complete equilibration of the melt and was then cooled to room temperature over a period of ~24 h, giving a cooling rate of ~1 °C/min. This yielded a clear glass rod ~1 cm × 3–4 cm that separated cleanly from the SiO_2, indicating that little, if any, attack of the SiO_2 tube had occurred. Indeed, the two Lewis acids are chemically incompatible and probably mix endothermically. Two separate boules were prepared in this manner to check for reproducibility.

Samples (~30 mg) for the DSC experiments were taken from the center of the boule and hermetically sealed into both aluminum and gold DSC sample pans in the anhydrous environment of the drybox. It was originally thought that gold pans would be required due to the reactivity of P_2O_5, but no difference in behavior in Au vs. Al pans could be observed. Data reported herein were obtained with aluminum sample pans. DSC scans were run at heating rates of 5, 10, 20, and 40 K/min, the lower limit being set by instrument sensitivity and the upper limit being set by thermal equilibration between sample and sample holder in the DSC. Some DSC samples showed irreproducible heating and cooling behavior and were discarded. After 5–10 cycles through the transition region, reproducibility in "good" samples was lost, presumably due to crystallization since heating above the melting point and quenching to room temperature brought back the glass transition at the correct value. In all, six different samples from each of the sealed tube preparations were studied and the agreement in T_g values was within ±2 K.

With samples that showed reproducible behavior at 10 K/min, variable heat/cool rate studies were performed in order to obtain a value of h^*, the activation energy for enthalpy relaxation. The sequence was[9] heat samples to T_g + 100 K, rate cool through the transition region at different rates to T_g − 100 K and reheat through T_g at the same rate. The calorimeter temperature was calibrated for each heating rate. (A variation of 4 K in the melting point of Pb (600.65 K) was found over the heating rate range 5–40 K.) Temperatures are believed accurate to ±0.5 K.

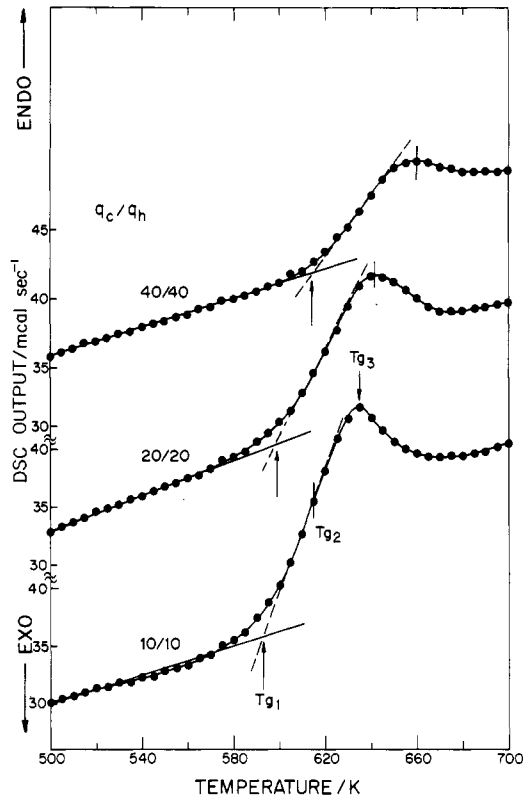

Figure 1. DSC scans of P_2O_5 glass at heating rates of 10, 20, and 40 K/min after cooling through the transition region at same rate. The 10/10 sample is larger than the other.

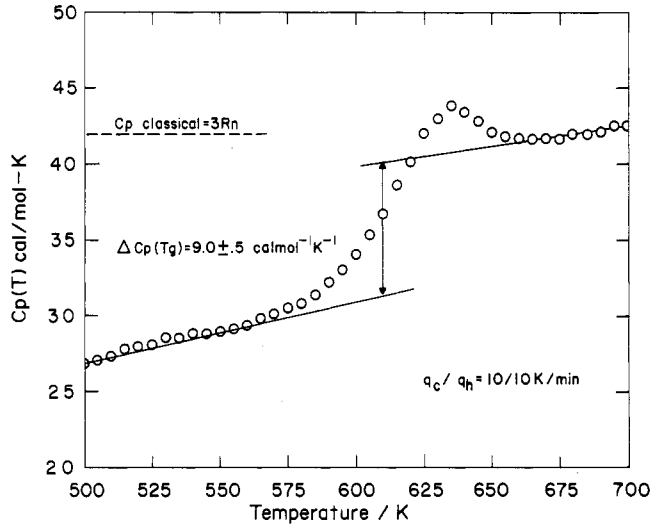

Figure 2. Heat capacity of P_2O_5 glass and supercooled liquid in the transition region. The change in C_p as T_g is 9.0 cal mol^{-1} K^{-1}. Heating rate for scan is 10 K/min.

Quantitative data for the heat capacity through the transition region were then obtained for one glass sample using a heating rate of 10 K/min. As a standard, α-Al_2O_3 of known mass and $C_p(T)$ was scanned under identical calorimeter conditions immediately after the heat capacity determinations for the glass. The heat capacities of P_2O_5 glass and supercooled liquid were then calculated directly by standard techniques.[10]

Results

DSC scans are given in Figure 1 for heating rates of 10, 20, and 40 K/min. These show onset T_g values of 591, 598, and 610

(4) Morey, G. W. *Properties of Glass*, 2nd ed.; Reinhold: New York, 1954.
(5) Moynihan, C. T.; Cantor, S. *J. Chem. Phys.* **1968**, *48*, 115.
(6) Adam, G.; Gibbs, J. H. *J. Chem. Phys.* **1965**, *43*, 139.
(7) Angell, C. A. In *Relaxation in Complex Systems* (Proceedings of the Workshop on Relaxation Processes, Blacksburg, VA, July 1983); Ngai, K., Smith, G. B., Eds.; National Technical Information Service, U.S. Department of Commerce: Washington, D.C., 1985; p 3; *J. Non-Cryst. Solids* **1985**, *73*, 1.
(8) Martin, S. W.; Angell, C. A. *J. Non-Cryst. Solids* **1984**, *66*, 429.
(9) Moynihan, C. T.; Easteal, A. J.; Tran, D. C.; Wilder, J. A.; Donovan, E. P., *J. Am. Ceram. Soc.* **1976**, *59*, 137.
(10) (a) O'Neill, M. J. *Anal. Chem.* **1966**, *38*(10), 1331. (b) Guttman, C. M.; Flynn, J. H. *Anal. Chem.* **1973**, *45*(2), 408.

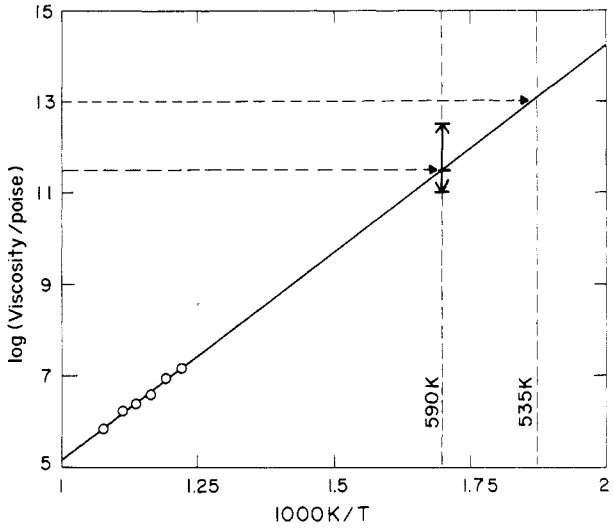

Figure 3. Viscosity–temperature relations for P_2O_5; data from ref 3. Solid line through data is a plot of eq 1. Dashed lines indicate that the viscosities $10^{11.5}$ and 10^{13} P are reached at 590 and 535 K, respectively.

TABLE I: Best Fit Parameters of Heating Rate Data to Eq 2

T_{g_i}	log A, kmin^{-1}	h^* kcal mol^{-1}	h^* kJ mol^{-1}	r, corr coeff
T_{g_1}	16.6	42.0	175.6	0.989
T_{g_2}	16.5	43.6	182.4	0.996
T_{g_3}	17.0	46.2	193.3	0.995
av (sd)		43.9 (2.1)	183.8 (8.9)	

K, respectively. The magnitude of ΔC_p (in units of mcal/s) is larger for the 10 K/min scan since these data were taken on a much larger sample. In Figure 2 are shown the heat capacity function and the value for the change in heat capacity at the glass transition, $\Delta C_p(T_g)$. $\Delta C_p(T_g)$ is found to be 8.9 ± 0.5 cal mol^{-1} K^{-1} or 1.27 cal g-atom^{-1} K^{-1}. Relative to C_p(glass), this value is typical for borosilicate glasses and smaller than for soda-lime glass.[11] However, it is larger than we expected on the basis of considerations given in the Discussion.

Combining Figure 1 and Figure 2 data, we conclude that T_g-(onset) for pure P_2O_5 based on enthalpy relaxation at 10 K/min is 590 ± 2 K or 319 °C, which is 57 °C, above the quoted value.[2] The discrepancy is due to the choice of T ($\eta = 10^{13}$ P) as the definition of the glass transition, since data on a variety of liquids suggest that T_g defined as in the Figure 1 DSC scans carried out at 10 deg/min occurs at values of viscosity that differ from liquid to liquid but fall in the range $10^{11.0}$–$10^{12.5}$ P. These relationships are shown in Figure 3, which indicates that η for P_2O_5 may indeed obey the Arrhenius law over the whole temperature range as assumed by Sakka and McKenzie.[2] The range of η at the DSC T_g does, however, allow for some curvature in the Arrhenius plot near T_g.

The interesting possibility that P_2O_5 is an ideal Arrhenius liquid can be checked by using the variable heating rate data seen in Figure 4 to obtain an activation energy for enthalpy relaxation to compare with that for viscosity. According to Moynihan et al.[9] for the cool/heat schedule used in acquiring the T_g data at different rates, a plot of log $|q|$ vs. $1/T_g$ (shown in Figure 4) yields the activation energy for enthalpy relaxation, h^*, according to

$$\frac{\mathrm{d}\ln|q|}{\mathrm{d}(1/T_g)} \approx \frac{-h^*}{R} \qquad (2)$$

Moynihan et al.[9] found that h^* obtained from such experiments coincides with the activation energy for viscosity measured in the same temperature range for three liquids of different chemical

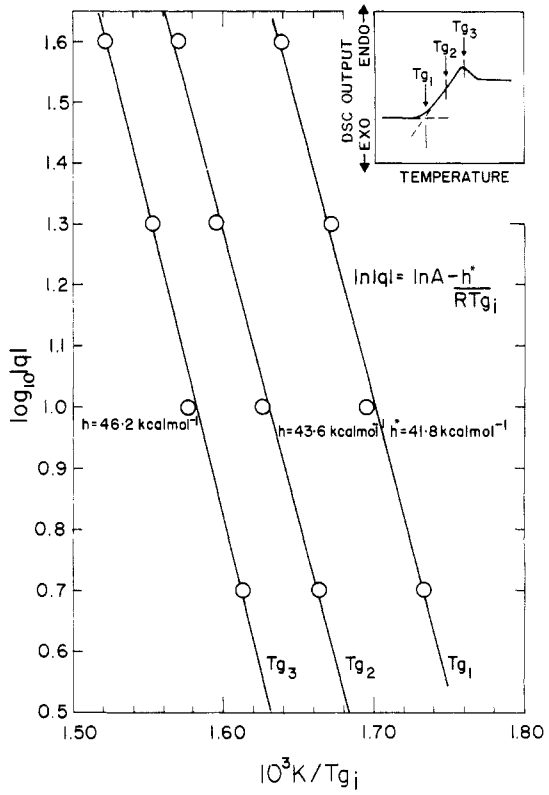

Figure 4. T_g for P_2O_5 measured at different heat/cool rates and defined as in the inset, plotted in Arrhenius form to yield[9] enthalpy relaxation activation energies.

TABLE II: Temperature Scaling Parameters for Figure 5

liquid	T_g (K)
P_2O_5	537.4
SiO_2	1446.0
GeO_2	818.0
$Na_2O{\cdot}2SiO_2$	713.0
$Na_2O{\cdot}P_2O_5$	555.0
$ZnCl_2$i	370.5
$69ZnCl_2{\cdot}31Py^+Cl^-$	275.0
$K^+Bi^{3+}Cl^-$ (K:Bi = 1:2)	332.0
$K^+Ca^{2+}NO_3^-$ (K:Ca = 3:2)	306.0

nature and a correspondence may therefore be expected in the case of P_2O_5 also. As seen in Figure 3 and Table I the mean value of the enthalpy h^* obtained from three different definitions of T_g, 43.9 kcal/mol, is only marginally greater than the activation energy for viscosity measured by Cormia and McKenzie at much higher temperatures, 41.5 kcal/mol. This can only be rationalized if the viscosity remains essentially faithful to eq 1 down to T_g.

Discussion

Arrhenius Viscosity. The confirmation of Arrhenius behavior for P_2O_5 over the whole temperature range down to T_g is of considerable interest. It leads us to classify P_2O_5, as did Cormia et al.[3] as a network liquid with a three dimensionally extensive covalent bonding scheme stabilizing the intermediate-range order in the liquid, viz. a "strong" liquid, to use the terminology recently proposed by one of us.[7] This structural characterization is consistent with the polymeric bonding scheme between phosphorus and oxygen atoms known to exist in crystalline P_2O_5.[12] However, the Arrhenius behavior is somewhat surprising in view of the fact that in P_2O_5 one of the four oxygens coordinating each P atom is doubly bonded and does not participate in the network bonding scheme. On this basis it might have been expected that pure P_2O_5 would behave more like silica to which a limited amount of

(11) (a) Hagerty, J. S.; Cooper, A. R.; Heasley, J. H. *Phys. Chem. Glasses* **1968**, *9*(2), 47; **1968**, *9*(4), 132. (b) Angel, C. A. *J. Am. Ceram. Soc.* **1968**, *51*, 117.

(12) (a) de Decker, H. C. J. *Recl. Trav. Chim. Pays-Bas* **1941**, *60*, 413. (b) MacFillavry, C. H.; de Decker, H. C. J.; Nijland, L. M. *Nature (London)* **1949**, *164*, 448.

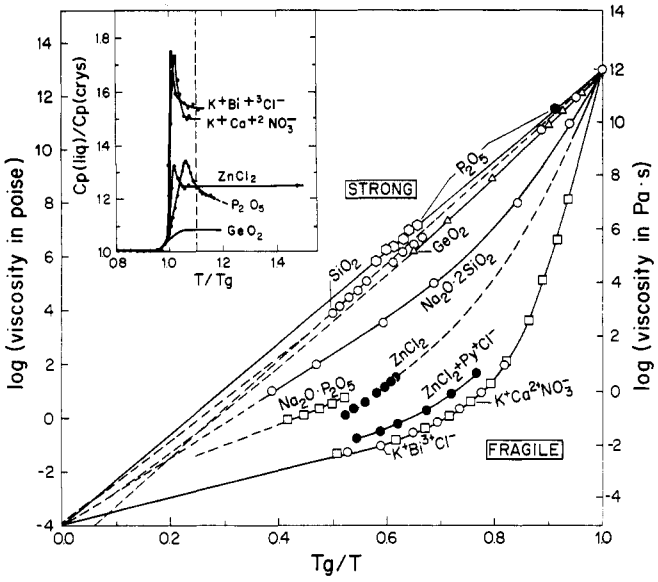

Figure 5. Viscosity vs. reduced temperature relations for various melts, showing the full range of observed behavior. Network (Arrhenius) liquids such as P_2O_5 and SiO_2 can be converted into non-Arrhenius liquids by added modifier, M_2O. Fully ionic liquids such as the molten salt mixtures KNO_3–$BiCl_3$ show the largest deviations from Arrhenius behavior. It is of note that the technologically interesting heavy metal fluorozirconate glasses also fall into this last category though data are not included here (however, see ref 7).

network-breaking oxide has been added, e.g., $Na_2O{\cdot}3SiO_2$. A possible stabilizing factor may be the freedom of the PO_4 group to rearrange its bonding electrons so that the oxygen that is doubly bonded is that which minimizes the local configurational energy.

In the main part of Figure 5 we show the relation of the P_2O_5 viscosity data to that of other representative liquids that have been used to establish the "strong" and "fragile" extremes of liquid behavior,[7] using the scaling parameters collected in Table II. Note particularly the positions of the sheet silicate $Na_2O{\cdot}2SiO_2$[13] and the chain structure $Na_2O{\cdot}P_2O_5$[14] on the one hand and the free ion extreme represented by $K^+Ca^{2+}NO_3^-$ on the other. It is seen that P_2O_5 stands out as an ideal or archetypal "strong" liquid case.

Heat Capacity Function and $\Delta C_p(T_g)$. The finding of Arrhenius viscosity behavior suggests that the configurational contribution to the heat capacity will be small, on the basis of both previous experience[6,7] and the Adam–Gibbs theory of transport processes in glass-forming liquids, which yields[5]

$$\eta = \eta_0 \exp(C/TS_c) \tag{3}$$

where S_c is the configurational entropy content of the liquid, (given approximately by $S_{\text{liquid}} - S_{\text{crystal}}$) and C is a constant. Any temperature dependence of S_c due to finite values of ΔC_p should thus lead to non-Arrhenius viscosity behavior. For comparison purposes, ΔC_p may be assessed as the value of $\Delta C_p(T_g)$/g-atom or, better, as the ratio of C_p for the supercooled liquid to C_p of the crystal, (or to C_p of the glass using short extrapolations of values beyond the transformation range). The appropriate extrapolation of the glass C_p for the present case, shown in Figure 3, is an upward sloping line consistent with the fact that the classical heat capacity of 42 cal/(mol deg) is far from being realized at T_g (partly due to the high Einstein temperature for the P=O bond; see below). The C_p ratio is shown as a function of T/T_g in Figure 5, insert, where it is compared with values for other glass-forming liquids with bonding schemes ranging from purely covalent to purely ionic. The surprising feature to us is the magnitude of the C_p(liq)/C_p(cryst) function for P_2O_5 above T_g, $\approx$1.2. This value is almost as large as for $ZnCl_2$ ($\approx$1.25) which is "intermediate" in the log η vs. T_g/T scheme of Figure 5. The actual magnitude of $\Delta C_p(T_g)$ is found from Figure 3 to be 9 ± 0.5 cal mol^{-1} K^{-1} or 1.29 cal g-atom^{-1} K^{-1}. While this is much less than the 2.70 cal g-atom^{-1} K^{-1} "universal" value proposed by Wunderlich[15] and also less than the value for the common glassformer B_2O_3, 2.1 cal g-atom^{-1} K^{-1}, it is considerably greater than the value found for other cases that show Arrhenius viscosity behavior, e.g., the network liquids GeO_2 (0.5 cal g-atom^{-1} K^{-1})[16] and BeF_2 (0.0 cal g-atom^{-1} K^{-1}).[17] A value of 1.11 cal g-atom^{-1} K^{-1}, not much less than our value for P_2O_5, has been attributed to SiO_2[18] though it is associated with some experimental uncertainty. To appreciate the concern, we discuss briefly the physical basis for expecting a smaller ΔC_p for P_2O_5 in view of its Arrhenius viscosity.

For SiO_2, BeF_2, and GeO_2 network liquids, computer simulation studies[19,20] have suggested that viscous flow occurs by a defect mechanism involving oxide jumping, a cooperative rearrangement mechanism being discouraged by the rigid, self-reinforcing, locally tetrahedral covalent bonding that opposes changes in the short- and the intermediate-range ordering with changing temperatures. The change in heat capacty at T_g reflects the additional energy needed to activate translational and rotational degrees of freedom (most vibrational modes become accessible far below T_g) and is larger in proportion to the number of new configurations that become available for each bond broken. Since the network bonding minimizes configurational degeneracy it seems reasonable that the measured $\Delta C_p(T_g)$ should be quite small for these liquids. On the other hand, in very non-Arrhenius liquids such as the well studied KNO_3 + $Ca(NO_3)_2$ glass-forming system,[21] the liquid structure can degrade rapidly with temperature since the network-bonding characteristics of SiO_2 and GeO_2 have now been replaced by nondirectional ionic bonding that allows many new particle arrangements for a given configurational energy input (excitation). Accordingly such liquids show a large change in C_p relative to the glass C_p at T_g. The magnitude of $\Delta C_p(T_g)$ should therefore be correlated with the extent of bond topological order that describes the short- and intermediate-range structure in the liquids.

The ideally Arrhenius behavior of P_2O_5 suggests the existence of a high degree of topological order in the liquid, and a very small ΔC_p value could therefore have been expected. The intermediate value of $\Delta C_p(T_g)$ found in this work could be interpreted as indicating that the measured $\Delta C_p(T_g)$ is due to some degradation of the P_2O_5 structure due to its hygroscopic nature, with OH groups in some way accounting for the extra ΔC_p. However, this would be inconsistent with the correct location of T_g and with the values of h^* in Figure 4, which should also be affected by H_2O uptake. Thus, to preserve eq 3, we must suppose that much of the configurational degeneracy introduced above T_g is somehow not available to assist in the relaxation of shear stress. In work to be presented we will show that ΔC_p actually decreases anomalously with initial additions of the modifier Li_2O to pure P_2O_5 toward values more typical of "strong" liquid behavior.

There is also a problem with the magnitude of the glassy-state heat capacity. C_p(glass) is far below the classical value of 6 cal g-atom^{-1} K^{-1} (3R) usually reached near T_g;[11] see Figure 2. Recalling that one of the oxygens of P_2O_5 is doubly bonded, it is reasonable to suppose that the P=O stretching mode is only weakly excited at T_g. If, accordingly, we assume n = 6, then the classical C_p would be 36 cal mol^{-1} K^{-1}, which is in the range found experimentally. For another case similar to P_2O_5 in this respect

(13) Fulcher, G. S. *J. Am. Ceram. Soc.* **1925**, *8*, 339.
(14) Callis, C. F.; Van Wager, J. R.; Metcalf, J. S. *J. Am. Chem. Soc.* **1955**, *77*, 1471. Debolt, M. A.; Easteal, A. J.; Macedo, P. B.; Moynihan, C. T. *J. Am. Ceram. Soc.* **1976**, *59*, 16.
(15) Wunderlich, B. *J. Phys. Chem.* **1960**, *64*, 1052.
(16) Angell, C. A.; Tucker, J. C. In *Chemistry of Process Metallurgy*, Jeffes, J. E. E.; Tait, R. J., Eds.; Institution of Mining and Metallurgy: London, 1974; p 207.
(17) Tamura, S.; Yokokawa, T. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 2542.
(18) Richet, P.; Bottinga, Y. *J. Non-Cryst. Solids* **1971**, *69*, 177; *Geochim. Cosmochim. Acta* **1984**, *48*, 453.
(19) (a) Woodcock, L. V.; Angell, C. A.; Cheeseman, P. A. *J. Chem. Phys.* **1976**, *65*, 1565. (b) Angell, C. A.; Cheeseman, P. A.; Phifer, C. C. *Proc. Symp. Mater. Res. Soc.*, in press.
(20) Brawer, S. A. *J. Chem. Phys.* **1981**, *75*, 3516.
(21) Rao, K. J.; Angell, C. A.; Helphrey, D. W. *Phys. Chem. Glasses* **1973**, *14*, 26.

we may refer to the nitrate glasses, in which the N–O bonds are of bond order 1.5 and in which C_p has reached only 70% of the classical value when T_g is reached.[21]

Conclusions

The value of the DSC-determined T_g of P_2O_5 has been found to be 590 ± 2 K for a heating rate of ≈10 K/min. The DSC T_g occurs when the liquid viscosity reaches a value of $10^{11.5}$ P and the combination of this value with existing viscosity data, supported by enthalpy relaxation data, indicates that P_2O_5 behaves in a strictly Arrhenius fashion with respect to the temperature dependence of viscosity. The value of ΔC_p at T_g for P_2O_5 (1.29 cal g-atom^{-1} K^{-1}) is smaller than for most liquids but larger relative to C_p(glass) than is expected from the Arrhenius behavior of the viscosity. The heating rate dependence of T_g has been used to determine the value for the enthalpy relaxation activation energy in the transition region and is found to be 43.9 ± 2.1 kcal/mol, essentially that of viscous relaxation. Further work analyzing the kinetics of enthalpy relaxation in pure P_2O_5 and comparing the alkali-modified glass behavior is in progress.

Acknowledgment. This work was carried out with the financial support of Department of Energy, Grant No. DE-FG02-84ER45. S.W.M. thanks the Sohio Foundation for providing a research fellowship during part of the period of this work.

Registry No. P_2O_5, 1314-56-3.