On the glass transition and viscosity of phosphorus pentoxide

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null
rameters in eq 1. Adopting the traditional idea that the viscosity of a liquid at its glass transition is $10^{11}$ \( \text{Pa}\cdot\text{s} \), one can calculate \( T_g \) 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 \( \approx 7 \) 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 \( \text{P}_2\text{O}_5 \) is an unusually strong network liquid, in which case correlations of transport and liquid thermodynamic properties suggest\(^7\) that it would provide a further example of a liquid with very small \( \Delta C_p \) 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" \( \text{P}_2\text{O}_5 \) glass samples and report the results herein.

**Experimental Section**

Anhydrous \( \text{P}_2\text{O}_5 \) from the same manufacturer and of the same purity used by Cormia et al.\(^3\) (Mallinckrodt, 98%) was placed into a flame-dried \( \text{SiO}_2 \) tube in the anhydrous environment of a high-quality drybox described previously.\(^4\) The tube was evacuated at room temperature to \( \approx 25 \mu\text{mHg} \) over a liquid \( \text{N}_2 \) 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 \( \approx 24 \) h, giving a cooling rate of \( \approx 1 \) °C/min. This yielded a clear glass rod \( \approx 1 \) cm × 3–4 cm that separated cleanly from the \( \text{SiO}_2 \), indicating that little, if any, attack of the \( \text{SiO}_2 \) 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 (\( \approx 30 \) 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 \( \text{P}_2\text{O}_5 \), 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 \( \pm 2 \) 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 \( \Delta H \), the activation energy for enthalpy relaxation. The sequence was\(^5\) 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/min.) Temperatures are believed accurate to \( \pm 0.5 \) K.

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, \( \alpha - \text{Al}_2\text{O}_3 \) 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 \( \text{P}_2\text{O}_5 \) 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 K.

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same temperature range for three liquids of different chemical

correspond to the Arrhenius law over the whole temperature range as
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The discrepancy is due to the choice of

Combining Figure 1 and Figure 2 data, we conclude that $T_g$-

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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, $\Delta C_v(T_g)$. $\Delta C_v(T_g)$ is found to be $8.9 \pm 0.5$ cal mol\textsuperscript{-1} K\textsuperscript{-1} or 1.27 cal g-atom\textsuperscript{-1} K\textsuperscript{-1}. Relative to $C_v(glass)$, this value is typical for borosilicate glasses and smaller than for soda-lime glass.\textsuperscript{11} However, it is larger than we expected on the basis of

considerations given in the Discussion.

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10 deg/min occurs at values of viscosity that differ from liquid
to liquid but fall in the range $10^{11.0}$–$10^{2.5}$ Pa. These relationships

are shown in Figure 3, which indicates that $\eta$ for P2O5 may indeed obey the Arrhenius law over the whole temperature range as

assumed by Sakka and McKenzie.\textsuperscript{2} The range of $\eta$ at the DSC

$T_g$ does, however, allow for some curvature in the Arrhenius plot near $T_g$

The interesting possibility that P2O5 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.\textsuperscript{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

\begin{equation}
\frac{d \ln [q]}{d(1/T_g)} \approx -\frac{h^*}{R} \tag{2}
\end{equation}

Moynihan et al.\textsuperscript{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 3. Viscosity-temperature relations for P2O5; data from ref 3.

Solid line through data is a plot of eq 1. Dashed lines indicate that the viscosities $10^{11.3}$ and $10^{13}$ Pa are reached at 590 and 535 K, respectively.

<table>
<thead>
<tr>
<th>TABLE I: Best Fit Parameters of Heating Rate Data to Eq 2</th>
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<tr>
<td>$T_h$</td>
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<tr>
<td>$T^*$</td>
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<tr>
<td>$T_1^*$</td>
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<td>$T_2^*$</td>
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<td>av (sd)</td>
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considerations given in the Discussion.

Combining Figure 1 and Figure 2 data, we conclude that $T_g$-

(onset) for pure P2O5 based on enthalpy relaxation at 10 K/min is $590 \pm 2$ K or 319 °C, which is 57 °C above the quoted value.\textsuperscript{2} This structural characterization is con-

sistent with the polymeric bonding scheme stabilizing the intermediate-range order in the liquid, viz. a “strong” liquid, to use the terminology recently proposed by one of us.\textsuperscript{1} This structural characterization is consistent with the polymeric bonding scheme between phosphorus and oxygen atoms known to exist in crystalline P2O5.\textsuperscript{12} However, the Arrhenius behavior is somewhat surprising in view of the fact that in P2O5 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 P2O5 would behave more like silica to which a limited amount of

nature and a correspondence may therefore be expected in the case of P2O5 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 P2O5 over the whole temperature range down to $T_g$ is of considerable interest. It leads us to classify P2O5, as did Cormia et al.\textsuperscript{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.\textsuperscript{1} This structural characterization is consistent with the polymeric bonding scheme between phosphorus and oxygen atoms known to exist in crystalline P2O5.\textsuperscript{12} However, the Arrhenius behavior is somewhat surprising in view of the fact that in P2O5 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 P2O5 would behave more like silica to which a limited amount of


network-breaking oxide has been added, e.g., Na2O-3SiO2. A possible stabilizing factor may be the freedom of the PO4 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 P2O5 viscosity data to that of other representative liquids that have been used to establish the "strong" and "fragile" extremes of liquid behavior, using the scaling parameters collected in Table II. Note particularly the positions of the sheet silicate Na2O2SiO3,13 and the chain structure Na2O.P2O4,14 on the one hand and the free ion extreme represented by K+Ca2+NO3- on the other. It is seen that P2O5 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 and the Adam-Gibbs theory of transport processes in glass-forming liquids, which yields

$$\eta = \eta_0 \exp(C/T_s)$$

where $S_s$ is the configurational entropy content of the liquid, (given approximately by $S_{liquid} - S_{crystal}$) and $C$ is a constant. Any temperature dependence of $S_s$ due to finite values of $\Delta C_p$ should thus lead to non-Arrhenius viscosity behavior. For comparison purposes, $\Delta C_p$ 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 universality to us is the magnitude of the $C_p(lq)/C_p(cryst)$ function for P2O5 above $T_g$, $\approx 1.2$. This value is almost as large as for ZnCl2 ($\approx 1.25$) which is "intermediate" in the log $\eta$ 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 $\pm$ 0.3 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 Wunderlich15 and also less than the value for the common glassformer B2O3, 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 GeO2 (0.5 cal g-atom$^{-1}$ K$^{-1}$)16 and BeF2 (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 P2O5, has been attributed to SiO218 though it is associated with some experimental uncertainty. To appreciate the concern, we discuss briefly the physical basis for expecting a smaller $\Delta C_p$ for P2O5 in view of its Arrhenius viscosity.

For SiO2, BeF2, and GeO2 network liquids, computer simulation studies $^{16,19}$ have suggested that viscous flow occurs due to defects involved with oxide jumping, a cooperative rearrangement mechanism being responsible for the high, self-reinforcing, locally tetrahedral covalent bonding that opposes changes in the short- and the intermediate-range ordering with changing temperatures. The change in heat capacity 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 KN03 + Ca(NO3)2 glass-forming system,22 the liquid structure can degrade rapidly with temperature since the network-bonding characteristics of SiO2 and GeO2 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 $C_g$ 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 P2O5 suggests the existence of a high degree of topological order in the liquid, and a very small $\Delta C_p$ 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 P2O5 structure due to its hygroscopic nature, with OH groups in some way accounting for the extra $\Delta C_p$. 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 H2O 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 $\Delta C_p$ actually decreases anomalously with initial additions of the modifier Li2O to pure P2O5 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$^{-1}$ (3F) usually reached near $T_g$11 see Figure 2. Recalling that one of the oxygens of P2O5 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 P2O5 in this respect

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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.\(^2\)

Conclusions

The value of the DSC-determined \( T_g \) of \( \text{P}_2\text{O}_5 \) has been found to be \( 590 \pm 2 \text{ K} \) for a heating rate of \( \approx 10 \text{ K/min} \). The DSC \( T_g \) occurs when the liquid viscosity reaches a value of \( 10^{11.5} \text{ poise} \) and the combination of this value with existing viscosity data, supported by enthalpy relaxation data, indicates that \( \text{P}_2\text{O}_5 \) behaves in a strictly Arrhenius fashion with respect to the temperature dependence of viscosity. The value of \( \Delta C_p \) at \( T_g \) for \( \text{P}_2\text{O}_5 \) (1.29 cal g-atom\(^{-1}\) K\(^{-1}\)) is smaller than for most liquids but larger relative to \( C_p(\text{glass}) \) 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 \( 43.9 \pm 2.1 \text{ kcal/mol} \), essentially that of viscous relaxation. Further work analyzing the kinetics of enthalpy relaxation in pure \( \text{P}_2\text{O}_5 \) and comparing the alkali-modified glass behavior is in progress.

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Registry No. \( \text{P}_2\text{O}_5, 1314-56-3 \).