mura, *et al.*,[6] have found that the initiation rate constant of the polymerization of styrene by Ph_3CSnCl_5 in 1,2-dichloroethane is $11.6 \times 10^{-2}\ M^{-1}\ min^{-1}$ at 30°. They have attributed the difference between their value and ours to the ionizing power of the metal halide.[23]

The most probable transfer reaction that can occur is the proton transfer from the active polymer chain to the monomer molecule by a bimolecular process. This leaves a terminal double bond in the dead polymer chain while the activated monomer molecule can start another chain

$$Ph_3CCH_2CHPh(CH_2CHPh)_nCH_2\overset{+}{C}HPhHgCl_3^- + PhCH{=}CH_2 \longrightarrow Ph_3CCH_2CHPh(CH_2CHPh)_nCH{=}CHPh + CH_3\overset{+}{C}HPhHgCl_3^-$$

This reaction was shown to be operative by molecular weight studies.[22]

Conclusion

The use of catalyst systems which produce well-characterized carbonium ions can lead to the possibility of evaluating the initiation rate constant, and thus gain further insight into the reaction mechanism.

(23) J. L. Cotter and A. G. Evans, *J. Chem. Soc.*, 2988 (1959).

Anionic Polymerization of Styrene in Tetrahydropyran

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ABSTRACT: The propagation reaction in the anionic polymerization of styrene in tetrahydropyran has been studied as a function of alkali metal counterion and concentration of active species. Conductance measurements were made on the systems also, enabling both the ion pair and polystyryl anion rate constants to be measured. The latter was found to be comparable with values found in other ethereal solvents. For the ion-pair constant some differences were found from previously published data.

The presence of three forms of the reactive species in the anionic polymerization of styrene in ethereal solvents is now well established.[1-5] The contributions to the reaction rate of the free anion and the ion pairs can be estimated by a comparison of conductance and kinetic measurements.[6,7] The determination of the relative contributions of contact and solvent separated ion pairs is less easy but some estimates have been made.[5,8] There are large differences in behavior between a solvent of moderate dielectric constant such as tetrahydrofuran (THF) and one of low dielectric constant such as dioxane. In particular the contributions of free anion and solvent separated ion pairs become negligible in the latter solvent, and the order of reactivity of ion pairs as a function of counterion is quite different from that in THF. It is of some interest to investigate solvents of intermediate dielectric constant to describe the transitional behavior. Quite detailed studies have been previously reported[4,8] in tetrahydropyran (THP, dielectric constant ~5.5) with sodium as counterion and the ion-pair rate constant has been reported for K^+, Rb^+, and Cs^+ [9,10] in THP and recently for Li^+.[11] This paper presents data on Li^+ and a reassessment of work with other counterions, together with an estimate of the reactivity of the free polystyryl anion.

Experimental Section

Apparatus. Modifications of the basic apparatus described earlier were used.[12] For lithium as counterion this only involved the replacement of the butyllithium bulb with one containing a low molecular weight polystyryllithium prepared in benzene and freeze dried. For the other alkali metals a small flask was joined to the side of the apparatus. Into this the required alkali metal could be distilled to form a film which was used twice, once to form a "living" polymer solution to wash out the apparatus and later to form the initiator solution. Three styrene bulbs were required for washing, initiator formation, and polymerization, respectively; the styrene was prepared as described previously.[13]

Reaction rates were all measured at 30.0° in a Cary-14 spectrophotometer which was provided with a temperature-controlled cell block of heavier construction than normally supplied for spectrophotometers. A subsidiary temperature-controlled air circulation system was used in addition, to maintain parts of the reaction vessel outside the cell block at

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(1) D. N. Bhattacharyya, C. L. Lee, J. Smid, and M. Szwarc, *Polymer*, **5**, 54 (1964).

(2) H. Hostalka, R. V. Figini, and G. V. Schulz, *Makromol. Chem.*, **71**, 198 (1964).

(3) T. E. Hogen-Esch and J. Smid, *J. Amer. Chem. Soc.*, **87**, 669 (1965); **88**, 307 (1966).

(4) W. K. R. Barnikol and G. V. Schulz, *Z. Physik. Chem.*, **47**, 89 (1965).

(5) T. Shimomoura, K. J. Tölle, J. Smid, and M. Szwarc, *J. Amer. Chem. Soc.*, **89**, 796 (1967).

(6) D. J. Worsfold and S. Bywater, *J. Chem. Soc.*, 5234 (1960).

(7) D. N. Bhattacharyya, C. L. Lee, J. Smid, and M. Szwarc, *J. Phys. Chem.*, **69**, 612 (1965).

(8) L. Böhm, W. K. R. Barnikol, and G. V. Schulz, *Makromol. Chem.*, **110**, 222 (1967).

(9) F. S. Dainton, G. C. East, G. A. Harpell, N. R. Hurwurth, K. J. Ivin, R. T. LaFlair, R. H. Pallen, and K. M. Hui, *Makromol. Chem.*, **89**, 257 (1965).

(10) F. S. Dainton, K. J. Ivin, and R. T. LaFlair, *Eur. Polym. J.*, **5**, 379 (1969).

(11) M. Van Beylen, M. Fisher, J. Smid, and M. Szwarc, *Macromolecules*, **2**, 575 (1969).

(12) D. J. Worsfold and S. Bywater, *Can. J. Chem.*, **38**, 1891 (1960).

(13) S. Bywater and D. J. Worsfold, *J. Phys. Chem.*, **70**, 162 (1966).

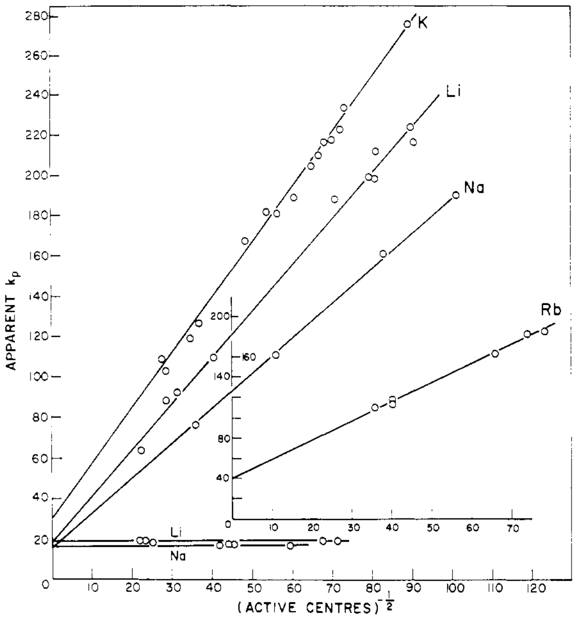

Figure 1. Apparent k_p ($-$d ln M/dt/[active centers]) as a function of counterion and concentration at 30°. Horizontal lines, values obtained in presence of tetraphenylboride salt.

operating temperatures. The reactions were normally monitored by following the disappearance of the styrene absorption at 291.2 mμ. In a few experiments at high initiator concentration where the rates were very rapid, the reaction was followed at 240–260 mμ where the styrene monomer absorption is stronger and so very dilute solutions could be used to avoid self-heating of the cell contents. The concentrations of active polystyryl salts were also determined spectrophotometrically using the styryl anion absorption band (λ_{max} Li 338 mμ; Na, 344 mμ; K, 342 mμ; Cs, 345 mμ). The extinction coefficients for several of the salts were measured by destroying part of the reactive centers with weighed amounts of t-butyl alcohol (ϵ_{Na} = 1.35 × 10^4, ϵ_K = 1.38 × 10^4, ϵ_{Cs} = 1.33 × 10^4 at the respective maxima). The differences are small, of the order of the experimental error, but appear to correlate with the half-width of the absorption band. An average value of 1.35 × 10^4 was used for all counterions.

The reaction cell could be modified to include a conductance cell. In this case the low molecular weight polystyryl salt normally used as initiator was used to study conductance. Its molecular weight varied between 1500 and 6000. Cell resistances were measured using a Wayne-Kerr universal bridge. Concentrations were measured spectrophotometrically and were varied by distillation of solvent. Similar techniques were used for the tetraphenylboride salts.

Tetrahydropyran (Matheson Coleman and Bell) was first refluxed over CaH_2 and ferrous ammonium sulfate or potassium metal and fractionated taking a middle cut. This fraction was again refluxed over potassium metal with or without added fluorenone and fractionated at high reflux ratio in a 100-plate column. The product was stored on the vacuum line over Na–K alloy. The density of THP at 30° was found to be 0.874 and its viscosity 0.755 cP.

Table I[a]

Summarized Results (T = 30°)

Salt	Λ_0	$k_p^- K_D^{1/2}$	K_D	k_p^-	$k_p^{\pm}$
Li^+Pst^-	40	2.25	1.9 × 10^{-10}	1.6 × 10^5	19.5
Na^+Pst^-	37	1.73	1.7 × 10^{-10}	1.3_5 × 10^5	17.0
K^+Pst^-	39.5	2.78	4.0 × 10^{-10}	1.4 × 10^5	30 ± 5
Rb^+Pst^-	47	1.90	3.7 × 10^{-10}	1.0 × 10^5	40 ± 5
$Li^+BPh_4^-$	57		2.07 × 10^{-6}		
$Na^+BPh_4^-$	53		2.19 × 10^{-6}		

[a] Units in moles, liters, and seconds.

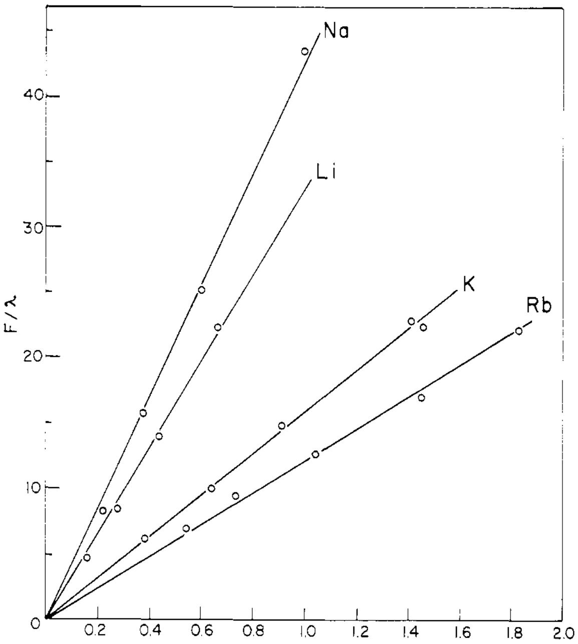

Figure 2. Equivalent conductance as a function of concentration with various counterions at 30°.

Sodium tetraphenylboride ($NaBPh_4$, Fisher Scientific) was recrystallized from ether–cyclohexane or tetrahydrofuran. $LiBPh_4$ was formed in THF by treatment of the sodium salt with analytical grade LiCl under vacuum. The precipitated salt was recrystallized under nitrogen from ether-cyclohexane. It appears to oxidize in solution quite rapidly. $KBPh_4$ was precipitated in aqueous solution from $NaBPh_4$ and analytical grade KCl. The washed filtrate was reprecipitated from acetone–water. The sodium salt is quite soluble in THP; the lithium salt is only sparingly soluble (7 × 10^{-4} M); the potassium salt almost insoluble ($\leqslant$3 × 10^{-5} M).

Results

Figure 1 shows the kinetic data plotted in the form reported by Szwarc and collaborators,[7] *i.e.*, as apparent k_p *vs.* [active centers]$^{-1/2}$. The intercept gives the total ion-pair rate constant, $k_p^{\pm}$ and the slope $k_p^- K_D^{1/2}$ (where k_p^- is the free anion rate constant and K_D the ion-pair dissociation constant). In order to increase the accuracy with which the ion-pair rate constant can be measured, some experiments were carried out (Li^+, Na^+) in the presence of the appropriate tetraphenylboride salt. The solubility in THP of $LiBPh_4$ is small, but from the determination of the dissociation constants of the polystyryl and tetraphenylboride salts, the concentration of Li^+ in a tetraphenylboride solution at near saturation is sufficiently high to suppress the ionization of polystyryllithium, so that the contribution to the polymerization rate from the free anion is negligible. No change in the spectrum of polystyryllithium in the presence of $LiBPh_4$ was noted with our preparation (*cf.* ref 10). The ion-pair rate constants were in this way found to be 19.5 (Li^+) and 17.0 (Na^+) (M^{-1} sec^{-1}). For potassium and rubidium only the extrapolation method can be used to determine the ion-pair constant which results in a larger uncertainty, $k_p^{\pm} = 30 \pm 5$ (K^+) and $k_p^{\pm} = 40 \pm 5$ M^{-1} sec^{-1} (Rb$^+$).

Figure 1 also allows the estimation of $k_p^{-}K_D^{1/2}$. The values are given in Table I. The only results available for comparison are those determined for polystyryllithium and sodium.[4,11] The values in Table I appear to be higher even after allowance for the temperature difference between these and earlier measurements. Conductance determinations on low molecular weight polystyryl salts enable estimates to be made of k_p^-. The conductance curves are shown in Figure 2 plotted according to the method of Fuoss.[14] Small corrections were applied to the data to normalize them all to a polymer degree of polymerization of 25, by assuming the anion mobility is inversely proportional to the square root of DP. To evaluate K_D, values are required for Λ_0. These were estimated using Walden's rule from the data previously reported in tetrahydrofuran.[5,7] As this procedure may produce small errors due to differences in degree of solvation between THF and THP, particularly for the lithium ion, the values for polystyryllithium and sodium were checked by determining Λ_0 of the tetraphenylborides in THP. These data together with use of Walden's rule on the (nonsolvated) anions enabled alternative values for Λ_0 of the two polystyryl salts to be obtained. Only small differences between the two methods were observed, of the order of the experimental error, and so an average value was used. No value exists for Λ_0 of polystyrylrubidium so an arbitrary value equidistant from those reported for the potassium and cesium salts in THF was converted using Walden's rule. The Λ_0 values and K_D values are given in Table I together with derived values of k_p^-.

Discussion

The variation of ion-pair rate constants with counterion is noticeably different from that in THF where the relative rates seem mostly to be determined by ease of formation of solvent separated ion pairs. The order of reactivity (with the exception of Li$^+$), Rb$^+$ > K$^+$ > Na$^+$, is much the same as in dioxane, as was previously noted[10] although our rate constants for K^+, Rb$^+$ are considerably lower.

The ion-pair rate constant for Na$^+$ agrees well with two values quoted in the literature (16.8 and 17.8 at 30°)[5] but not with the more recent one of <5 (M^{-1} sec^{-1}). We cannot confirm the suggestion[11] that the rate constant is different when determined by extrapolation to high concentration from that determined by supression of ionization. For the sodium compound, good agreement is reached between the two methods. For the lithium compound (where $k_p < 5$ was also reported[11]) the scatter of results is unfortunately larger and most reliance has been placed on the salt supression experiments to determine the ion-pair constant, but again the extrapolation of the rates obtained in the absence of added salt would seem to be inconsistent with a rate constant less than five. For potassium and rubidium counterions, however, the difference between the present and earlier results[10] is best explained by the use of the two different techniques, because, according to our experiments, the tetraphenylborides are insufficiently soluble in THP to suppress ionization completely. This cannot be the explanation for the differences with the lithium and sodium salts, for they are sufficiently soluble.

It seems likely that a higher contribution from more reactive solvent-separated ion pairs is responsible for the slightly higher rate constant of the lithium compound compared with the sodium one, although the effect is much smaller than in THF. The presence of a small contribution from solvent-separated ion pairs has been suggested even for the sodium compound[8] in THP, so it would be expected to be higher for lithium.

A few attempts were made to measure the propagation constant for polystyrylcesium but the results resembled those found previously in tetrahydrofuran.[7] The ion-pair rate constant evaluated was quite high ($\sim$70 M^{-1} sec^{-1}) and the value of $k_p^{-}K_D^{1/2}$ much lower than with the other alkali metals. The k_p^- value obtained was therefore anomalously low. Such effects have been attributed[7] to the presence of intramolecular triple ions. Attempts to eliminate this phenomenon by producing "single-ended" polystyrylcesium in THP *via* alkali metal cleavage of cumyl methyl ether were not successful, apparently because the cesium alkoxide coprecipitated on cooling the solution and alkoxide free cumylcesium could not be produced. These results raise the question whether this effect is not partly present with polystyrylrubidium and hence the measured ion-pair constant is a maximum value. The measured free anion rate constant is lower than for the other alkali metals. The difference is, however, little greater than the probable experimental error and further uncertainty arises because the estimate of Λ_0 is far less reliable than for the other compounds. Under these conditions, it is impossible to make a decision on this point although any effect must be much smaller than with cesium as counterion.

The free anion rate constant ($k_p^- \sim 1.3 \times 10^5$ M^{-1} sec^{-1} at 30°) is in general comparable with other values reported in cyclic ethers. In tetrahydrofuran at 25° various values have been reported depending on experimental techniques and data treatment, 6.5×10^4,[7] 8×10^4,[2] and 1.3×10^5.[15] The value at 30° would be expected to be about 35% higher. Recent results in hexamethylene oxide at 30° give a value of 10^5.[16] As the probable error in these determinations is likely to be around 30% there is no discernible trend of this rate constant with solvent.

The variation of K_D with counterion in THP is noticeably different from that in THF, where its value decreases with increasing counterion radius by a factor of about 30 along the series of alkali metals. All the dissociation constants measured in THP are similar, within a factor of 2, which is not much larger than the probable error of the measurements. It would seem likely that a rough balance has been reached between the effect of strong specific cation solvation, which tends to favor higher dissociation with smaller counterions, and coulombic interaction which acts in the opposed sense.

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(14) R. M. Fuoss, *J. Amer. Chem. Soc.*, **57**, 488 (1935).

(15) H. Hostalka and G. V. Schulz, *Z. Physik. Chem.*, **45**, 286 (1965).

(16) G. Loehr and S. Bywater, *Can. J. Chem.*, in press.