Kinetics of the Reaction of Poly-α-methylstyryl Sodium and Potassium with t-Butyl Chloride in Dioxane

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ABSTRACT

The kinetics of the reaction of "living" poly-α-methylstyrene with t-butyl chloride has been studied spectrophotometrically in dioxane for the counterions sodium and potassium. The reactions are found to be precisely first-order with respect to both species. The Arrhenius parameters are determined for the overall ion-pair reaction with t-butyl chloride; the living ends have been shown to exist largely in the form of contact ion-pairs. The gaseous products of the reactions are quantitatively estimated by GLC analysis, and in the case of the sodium-initiated system, Arrhenius parameters are recovered for the elimination reaction. A tentative mechanism is advanced to explain the kinetic data.

INTRODUCTION

The effect of cation pairing upon the reactivity of carbanions in solution has been demonstrated [1-3]. These studies have shown that cation pairing might, in some cases, depending on the solvent and

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cation, enhance or reduce the rate of polymerization. Similarly, Baker and East [4] have shown that, when termination reactions were isolated by deliberately adding a terminating agent such as t-butyl chloride, after polymerization was complete, the ion-pair rates were enhanced or reduced depending on solvent and cation pairing. Moreover, preliminary studies for the system Ps^- Na^+/dioxane/t-BuCl by the same authors have shown that the observed first-order rate constants, obtained at various initial t-butyl chloride concentrations, were linearly dependent on the t-butyl chloride concentration. Also, the rates were shown to be affected by alkyl halide structure; the n-butyl and secondary halides reacted at a faster rate than t-halides. The work described in the present paper is an extension of the investigation begun by Baker and East. Additionally, a comparison of this work with that published on the polystyryl system should throw some light on the influence of anion structure on the rate of reaction and also lead to a better understanding of the mechanism of such reactions.

EXPERIMENTAL

All reagents were rigorously purified, and the final stages of the purification of the monomer and solvent, the preparation of the initiating solutions, and the filling of the reaction cell were carried out under vacuum on a vacuum line. All transfers of material under vacuum were carried out using breakseals, and the reactions were performed in all-glass apparatus.

"Living" polymer solutions were prepared by contact between a mixture of α-methylstyrene (1-2 cm^3) in dioxane (110-120 cm^3) and the appropriate metal mirror for 3-4 h, by which time the desired "living" end concentration had been reached as judged by the color.

The kinetics of the termination reactions were followed spectrophotometrically in a constant temperature bath fitted inside the cell compartment of a S.P. 500 spectrophotometer. Measurements of optical density at a fixed wavelength in the range of 400-600 nm were carried out and the optical density reading relative to water was taken during a run. At the end of a run a blank reading relative to water was also taken. Details of the technique are described elsewhere [5].

Chloride Ion Determination

At the end of a run the reaction vessel was opened to air and 5 cm^3 aliquots of solution pipetted from the vessel into conical flasks (250 cm^3) fitted with ground glass joints. To each 5 cm^3 quantity was added aqueous sodium hydroxide (10 cm^3; 7% w/v). The mixture was then vigorously shaken, stoppered, and allowed to stand for 24 h at room

temperature. After this time, complete hydrolysis of the t-butyl chloride had taken place, as shown by trial experiments. After neutralization with powdered analar calcium carbonate, the solution was titrated for chloride ions by Mohr's method [6].

RESULTS

The initial "living" end concentrations were 8-20 $\times$ 10^4 $\underline{M}$ throughout this work. Stability tests on the sodium and potassium initiated "living" end solutions indicated that they were not being "killed," other than by reaction with t-butyl chloride, during the time span of a run.

Using a large excess ($\sim$ 100-fold) of t-butyl chloride, the individual reaction-time curves followed a first-order law over a period of at least 4 half-lives and were analyzed by plotting log $(D_t - D_\infty)$ against time (t), where D_t and D_∞ are the optical density readings at time t and at infinite time, respectively (Fig. 1). The pseudofirst-order rate constants, k_1, were calculated from the slopes of log $(D_t - D_\infty)$ vs time plots. Concordant results were obtained whether the reaction was followed at 339 nm (λ_{max}) or 560 nm, the latter being more convenient at high "living" end concentrations.
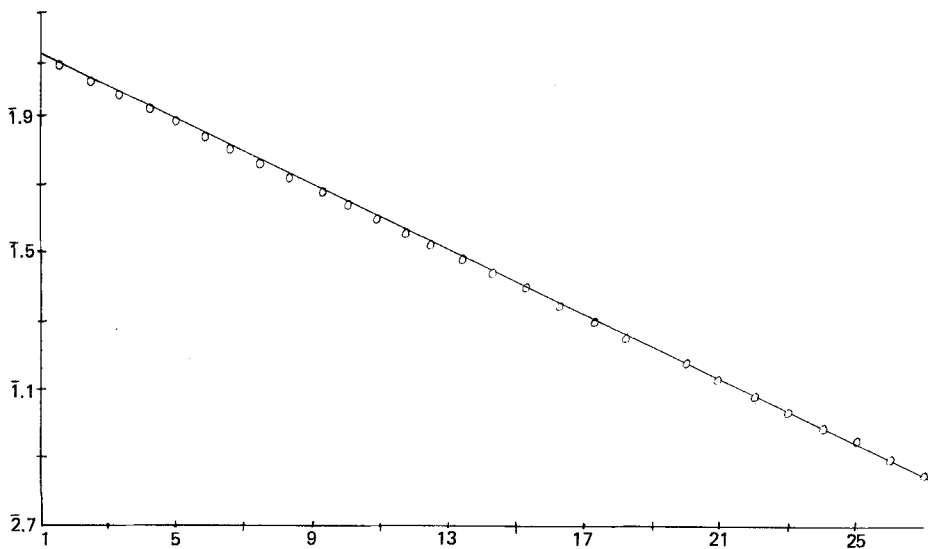

FIG. 1. Log $(D_t - D_\infty)$ vs time plot for a typical run. Abscissa: Log $(D_t - D_\infty)$. Ordinate: Time (min).

TABLE 1. Kinetic Results for the System $\alpha^- Na^+/Dioxane/t-BuCl$, $[LE] = 8-20 \times 10^{-4}$ $\underline{M}$

Run no.	T (°C)	$10^2 k_1$ (s^{-1})	[t-BuCl] ($\underline{M}$)	$10^2 k_t$(L m^{-1} s^{-1})[a]
42	12	0.104	0.209	0.497
44	12	0.078	0.148	0.526
46	12	0.041	0.081	0.503
				0.508 ± 0.02[b]
3	20	0.161	0.156	1.03
8	20	0.143	0.144	0.990
20	20	0.148	0.145	1.01
				1.01 ± 0.02
50	30	0.235	0.114	2.06
58	30	0.376	0.171	2.20
59	30	0.134	0.069	1.94
60	30	0.128	0.064	1.99
				2.05 ± 0.11
33	40	0.308	0.073	4.47
38	40	0.605	0.124	4.87
39	40	0.382	0.082	4.65
40	40	0.504	0.110	4.58
				4.64 ± 0.17

[a]k_t = rate constant for termination.

[b]The errors quoted are the standard deviation.

The observed first-order rate constants obtained at various initial t-butyl chloride and "living" end concentrations for the Na and K initiated systems at 10, 20, 30, and 40°C are given in Tables 1 and 2. The plots of the variation of k_1 with t-butyl chloride concentration at the temperatures quoted above are shown in Figs. 2 and 3. The absence of intercepts bears out the fact that the "living" end solutions were quite stable (even at 40°C) before the addition of t-butyl chloride at the start of a run. Moreover, the plots show that the pseudofirst-order rate constants were directly proportional to t-butyl chloride concentration at all temperatures from 12 to 40°C, so that the

TABLE 2. Kinetic Results for the System $\alpha^- K^+$/Dioxane/t-BuCl

Run no.	T (°C)	$10^2 k_1$ (s^{-1})	[t-BuCl] ($\underline{M}$)	$10^2 k_t$ $(L\ m^{-1}\ s^{-1})$
41	12	0.094	0.209	0.448
43	12	0.065	0.151	0.430
47	12	0.043	0.095	0.453
				0.443 ± 0.01
22	20	0.049	0.056	0.880
36	20	0.147	0.167	0.880
37	20	0.051	0.060	0.850
35	20	0.068	0.076	0.890
				0.875 ± 0.02
48	30	0.061	0.038	1.59
51	30	0.189	0.117	1.60
52	30	0.252	0.160	1.59
				1.59 ± 0.01
54	40	0.373	0.111	3.36
55	40	0.224	0.066	3.40
57	40	0.181	0.054	3.36
				3.37 ± 0.02

reactions were all first-order with respect to both "living" ends and t-butyl chloride.

The plots of log k_t, where k_t is the termination rate constant, against $10^3 K/T$ are shown in Fig. 4, the data for which are tabulated in Table 3. The lines were drawn using the method of least squares, and the activation energies for termination (E_t) and frequency factors (A_t) were computed. The values obtained were E_t = 55.1 ± 0.3 kJ/mol, A_t = 8.30 ± 0.2 L m^{-1} s^{-1} and E_t = 52.4 ± 0.3 kJ/mol, A_t = 7.27 ± 0.2 L m^{-1} s^{-1} for the Na and K systems, respectively.

Attempts were made to prepare the lithium and cesium initiated polymer solutions by contact on the respective metal mirrors and when that proved unsuccessful, by initiation through the lithium and cesium naphthalides. Although the characteristically colored "living" end solutions were obtained using both methods of initiation, the "living" ends were not stable enough to allow kinetic measurements.
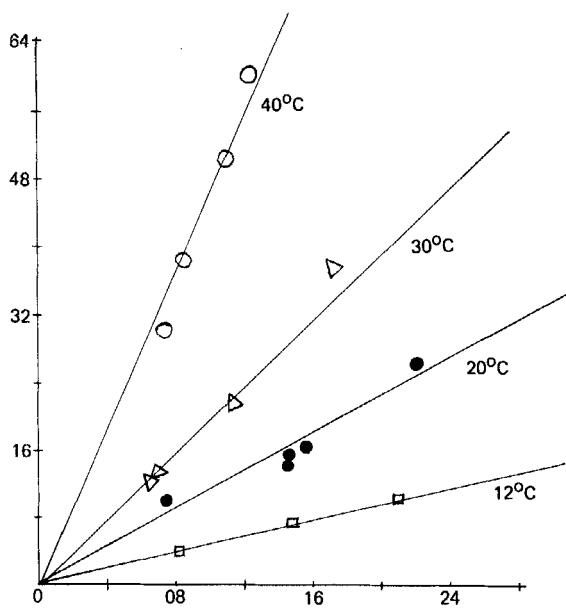
FIG. 2. $\alpha^- Na^+$/dioxane/t-BuCl. Abscissa: $10^2 \, k_1 \, (s^{-1})$. Ordinate: [t-BuCl], $\underline{M}$.
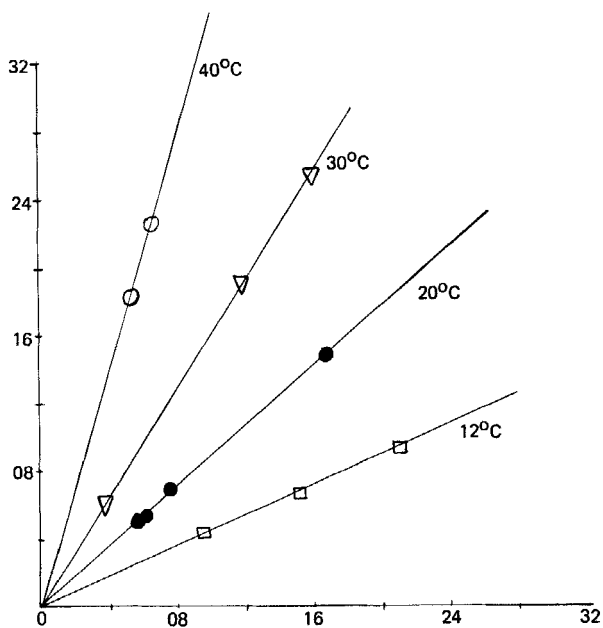
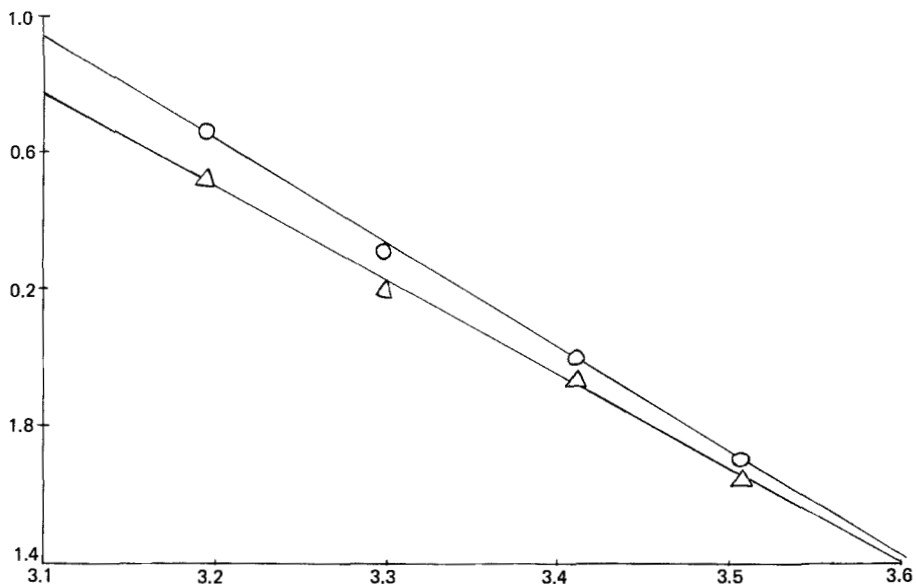FIG. 3. $\alpha^- K^+$/dioxane/t-BuCl. Abscissa: $10^2 \, k_1 \, (s^{-1})$. Ordinate: [t-BuCl], $\underline{M}$.

FIG. 4. Arrhenius plots of α^-Na$^+$, K$^+$/dioxane/t-BuCl. Abscissa: $2 + \log k_t$ (L m^{-1} s^{-1}). Ordinate: 10^3 K/T. ($\circ$) Na$^+$; ($\triangle$) K$^+$.

TABLE 3. Arrhenius Data

T (°C)	10^3 K/T	$10^2 k_t$ (L m^{-1} s^{-1})	$2 + \log k_t$ (L m^{-1} s^{-1})
		α^-Na$^+$/Dioxane/t-BuCl	
12	3.507	0.508 ± 0.02	1.7064
20	3.411	1.01 ± 0.02	0.0056
30	3.298	2.05 ± 0.11	0.3111
40	3.193	4.64 ● 0.17	0.6667
		α^-K$^+$/Dioxane/t-BuCl	
12	3.507	0.443 ± 0.01	$\overline{1}$.6464
20	3.411	0.875 ± 0.02	$\overline{1}$.9420
30	3.298	1.59 ± 0.01	0.2014
40	3.193	3.36 ± 0.02	0.5263

The inherent instability of the Li initiated system might be explained by side reactions such as isomerization and/or reaction with solvent to produce "dead" polymer [7, 8]. In the case of the Cs initiated system, it would appear from the molecular weight analysis of the insoluble material that only long-chain "living" end species were soluble in dioxane while the dimer and tetramer were insoluble.

Molecular Weight Effects

As previously described, the "living" end solutions were prepared by contact on the metal mirror for 3-4 h at room temperature. Solutions produced in this way, when terminated with water at room temperature, gave a polymer with a molecular weight of approximately 480. Since the theoretical molecular weight of the tetramer is 472, it can be assumed that in these solutions the tetramer predominates. When the solutions were stored in a refrigerator at $-30°C$ for several days and then warmed up to room temperature and terminated with water, the molecular weight was found to be 3600. When the stored solutions were warmed up to $40°C$ for 3-4 h and then terminated with water, the molecular weight fell to 700. Thus the polymer undergoing termination will, in most cases, be of molecular weight 700-3500 depending on the time the solution was stored and how long the solution was handled at room temperature before reaction. Though some freshly prepared solutions, when terminated with t-butyl chloride, were essentially tetramers, no variations in k_t were noted over this molecular weight range.

DISCUSSION

The reactions of "living" poly-α-methylstyryl sodium and potassium with t-butyl chloride in dioxane were first order with respect to "living" ends and t-butyl chloride concentration over the concentration range studied. Although ion-pairs involving smaller counterions may be solvated in dioxane, there is no evidence of free ions or solvent-separated ion-pairs. Thus Smid et al. [9] have found only contact ion-pairs of fluorenyl lithium in dioxane. Conductivity studies by Szwarc et al. [10] of polystyryl sodium in dioxane indicate no significant concentrations of free ions. One possible explanation is that the chair form of the dioxane molecule is not as likely to solvate cations as the boat form in which the oxygen atoms are in a more favorable conformation for solvation. Therefore, the chair form does not favor the formation of solvent-separated ion-pairs, and hence solvation by the dioxane molecule is only peripheral. It would appear that the chair form is predominant in these systems.

It must therefore be concluded that the rate constants obtained refer to attack of the contact ion-pairs on t-butyl chloride.

Reaction Product Analysis

The reaction of sodium and potassium initiated poly-α-methyl-styryl "living" ends with t-butyl chloride is expected to result in elimination or substitution, or both reactions may be in competition. Such a conclusion follows from the studies of Ingold [11] and others on the reaction of strong bases with alkyl halides. However, when the gaseous reaction products were analyzed by GLC analysis, the gases found were isobutene, as expected, and surprisingly, measurable quantities of isobutane [12]. Analysis of the solid reaction product was also surprising; apart from the expected hydrogen-ended and t-butyl-ended polymer, there was evidence of a new grouping in the terminated polymer which absorbed UV radiation in the 315-320 nm region. This 315-320 nm UV-absorbing grouping was absent in the polymer terminated by water and was therefore identified as a reaction product. Bearing in mind the simple kinetics observed, it seems clear that whatever complications arise in the nature of the products, the reactions involved are all probable simple bimolecular reactions involving "living" ends and t-butyl chloride.

A tentative mechanism has been advanced to explain the surprising presence of the 315-320 nm grouping and isobutane. When the reactants come together, ionic elimination and substitution processes may occur, accompanied by a side reaction operating through a radical or metal halogen exchange mechanism or through a hydride ion intermediate [13]. There is as yet no concrete evidence to support this argument, but it seems reasonable in view of the simple kinetics observed. Alternatively, the overall reaction could be a single-election transfer step, and the rate constant for this single process and the products of the reaction would be governed by the reactions occurring after this initial step. If one accepts the mechanism to be one of competing ionic processes plus metal-halogen exchange, then values for k_e, the rate constant for elimination, can be extracted from the data at each temperature and also the activation energy, E_e, and $\log A_e$ (frequency factor) for elimination.

The results of the GLC analysis of the gaseous products for the system $\alpha^- Na^+$/t-butyl chloride/dioxane are tabulated in Table 4. The isobutene figures are corrected, as shown in Table 4, because, for every mole of isobutane produced, 1 mol of isobutene is also produced. If percentage elimination is therefore to be calculated, %(isobutene) - %(isobutane) is a measure of the reaction. From these figures the overall rate constant, k_t, can now be split to give a rate constant for elimination (Table 5). The results show that as the temperature is increased from 12 to 40°C, the percentage of the reaction which occurs by elimination decreases. The rate constant for substitution (k_S) could not be computed because the extent of elimination and substitution did not add up to 100% because of other reactions forming isobutane and the 315-320 nm UV absorbing grouping in the polymer.

TABLE 4. GLC Analysis of Gaseous Products from the Reaction of $\alpha^- Na^+$ with t-BuCl in Dioxane

T ($^\circ$C)	% isobutene	% isobutane	Corrected value for % isobutene
12	78	2.0	76.0
30	64	2.5	61.5
40	42	4.0	38.0

TABLE 5. Data for Splitting Rate Constants: $\alpha^- Na^+$/Dioxane/t-BuCl

T ($^\circ$C)	$10^2 k_t$ (L m^{-1} s^{-1})	E^a	$10^2 k_e$ (Lm^{-1} s^{-1})
12	0.508	0.760	0.386
30	2.05	0.615	1.26
40	4.64	0.380	1.76

E^a = fraction of reaction occurring by elimination.

The NMR spectrum of the terminated polymer did show, however, an increase in the t-butyl groups with increasing temperature.

The Arrhenius plot of k_e versus 10^3 K/T is shown in Fig. 5. From the line drawn, the activation energy for elimination is 43.5 kJ/mol and the corresponding frequency factor, $10^{3.59}$ Lm^{-1} s^{-1}. While the plot is disappointing, it does confirm the general trend observed from the product analysis that elimination occurs with a lower activation energy than substitution. These findings are at variance with those given by Ingold for the reactions of bases with alkyl halides where the activation energy for substitution is generally lower than that for the corresponding elimination reaction [11]. A possible explanation for this difference is that, whereas Ingold's bases are generally small, one is dealing here with large polymeric carbanions and so steric factors become more important, retarding substitution. In addition, the carbanions are much stronger bases than those used by Ingold so that proton abstraction could be expected to be more competitive with substitution.

It should be noted that the resolving of the overall rate constants into the individual rate constants for elimination is based on the assumption that elimination is one of a group of competing reactions and that the corrected isobutene yield at each temperature does measure the extent of elimination. If it should become clear that the mechanism is of some other type (for example, electron transfer),
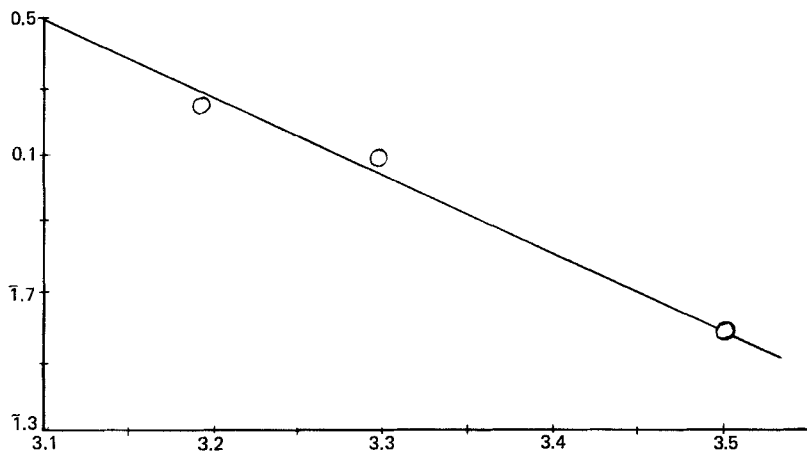
FIG. 5. Arrhenius plot for elimination in α^- Na$^+$/dioxane/t-BuCl. Abscissa: $2 + \log k_e$ (L m^{-1} s^{-1}). Ordinate: 10^3 K/T.

then the overall analysis would not be valid; equally, if isobutene were to be partially consumed in other reactions, corrections would be necessary.

A similar analysis of the potassium system was not attempted due to the uncertain reaction mechanism but, from the results obtained at 40°C, where 61% isobutene and 30% isobutane were the volatile products (compared to 42 and 4%, respectively, in the sodium system), it would appear that this system has a greater tendency for elimination than is the case for Na$^+$.

The termination process shows only a small variation on changing the counterion from Na$^+$ to K$^+$. This would suggest that only a small separation of the ions occurs on forming the transition state, though it is noticeable that the activation energy is higher in the case of Na$^+$.

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