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ANIONIC POLYMERIZATION OF STYRENE IN TETRAHYDROFURAN (THF) WITH CUMYLCAESIUM AS INITIATOR

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Abstract—The kinetics of the anionic polymerization of styrene initiated by cumylcaesium have been reinvestigated in tetrahydrofuran. Quite unlike earlier investigations, the ion pair rate constant $\bar{k}_{p(\pm)}$ was found to be 130 l/mole/sec at 25° and the dissociation constant of polystyrylcaesium to be about 5×10^{-10} mole/l. In the presence of caesiumtriphenylcyanoborate used as a common ion salt addition, $\bar{k}_{p(\pm)}$ was measured over a wide range of temperature. The results are compared to the temperature behaviour of the ion pair rate constants obtained with polystyrylsodium in polar solvents; they indicate that the existence of solvent separated ion pairs cannot be excluded for polystyrylcaesium.

I. INTRODUCTION

In kinetic investigations of the anionic polymerizations of polar monomers, e.g. 2-vinyl-pyridine [1] or methylmethacrylate [2, 3], the use of caesium organic compounds as initiators provides the advantage of a polymerization process simpler than for the correspondent sodium compounds. This is mainly due to the reluctance of the larger caesium ion to become strongly solvated either by the solvent or by the polar groups of the monomer and of the polymer being formed. It is of some interest to compare the kinetic results for polar monomers with those obtained for nonpolar monomers, especially with those for styrene because the anionic polymerization of this monomer has been thoroughly investigated with different gegenions [4] in a series of solvents [5, 6].

Thus, the kinetic behaviour of polystyrylcaesium has been characterized by Szwarc *et al.* for the solvents dimethoxyethane (DME) [7], tetrahydrofuran (THF) [8–10] and dioxane (DO) [10], and by Ivin *et al.* for tetrahydropyrane (THP) [11]. In distinction to polystyrylsodium, in all these studies the formation of differently reactive types of ion pairs could not be established in accordance to spectroscopic and conductometric measurements of similar caesium compounds [12–14], where the existence of different types of ion pairs could not be revealed either. Therefore, the rate constant $\bar{k}_{p(\pm)}$ for the ion pair obtained either by extrapolation to infinite concentration of the active centres or by suppression of the dissociation of the active centres by sufficient $Cs(BPh_4)$ as a common ion salt, was referred to the rate constant $k_{p(\pm)c}$ of the contact ion pair of polystyrylcaesium.

The rate constants determined in the solvents mentioned above, however, seem to be inconsistent for they do not correlate to the solvation ability of the solvent in contrast to the behaviour of polystyrylsodium [6, 15, 16]. Thus, $\bar{k}_{p(\pm)}$ is reported to be about 150 in DME [7] and 50 l/mole/sec in THP [11] at 25°, whereas the smaller value of about 25 l/mole/sec was found in both THF [8] and DO [10] at the same temperature. Besides this somewhat surprising result, an abnormally low frequency factor of about 10^5 has been reported for the rate constants $\bar{k}_{p(\pm)}$ in the solvents so far investigated [7–11]. This value is by three powers of 10 smaller than that observed for the individual rate constants of all three differently reactive species of polystyrylsodium [6, 15].

Since these findings are not easy to understand, we reinvestigated the kinetics of polystyrylcaesium in THF; in particular, the rate constant $\bar{k}_{p(\pm)}$ was measured between +30 and −80°. These measurements were performed in the presence of caesiumtriphenylcyanoborate, $Cs(BPh_3CN)$, which already has been used to provide a common ion in the anionic polymerization of methylmethacrylate [2, 3]. Therefore, it also is desirable to confirm this salt to be appropriate for that purpose.

II. EXPERIMENTAL

The technique was as described earlier [8, 17]. To avoid the delicate manipulation of fragile bulbs containing the monomer, the basic apparatus was simplified so that the monomer could be repeatedly added as an approx 0·1 M solution in THF by a burette which was connected to the reaction vessel via a greaseless valve. After the monomer solution had been directly distilled into the burette from a commonly used vacuum line, the reaction vessel (in principle, a glass tube with an optical cell) was connected via another greaseless valve to a vacuum apparatus in which the initiator (cumylcaesium) was prepared. After filling the reaction vessel with sufficient initiator solution of the desired concentration, the reaction vessel and the monomer burette were put under slight pressure of purified nitrogen to allow for possible leakage of the valves.

Polymerization rates were measured in a Beckman spectrophotometer Acta CIII by following the disappearance of the styrene absorption at 291·5 nm. The concentration of polystyrylcaesium, monitored during the reaction by its absorption at 343 nm, was calculated with an extinction coefficient of $1{\cdot}35 \times 10^4$ cm^2 mol^{-1} at 25° which seems to be the most plausible value at present [4, 5, 7, 11]. It was shown that the extinction coefficient does not vary with temperature.

In all experiments, good first order plots with respect to the monomer were observed and rate constants were calculated. Experiments performed in absence of the common ion, however, yielded reproducible results only with freshly prepared initiator. A repeated addition of monomer to the completely converted reaction solution led to poorly reproducible and smaller values for the rate constant $\bar{k}_p$. This is due to a slow decomposition of polystyrylcaesium resulting in the production of a dissociable compound which partially suppresses the dissociation of the active centres. Assuming first order decay, the decomposition rate constant for polystyrylcaesium is 2–3 × 10^{-4} $\sec^{-1}$ in THF at 25°.

Below room temperature, experiments were performed in a quartz Dewar filled with methanol and provided with optical windows. It could be maintained at the required temperature within 0·1° by a cryostat. The temperature was controlled by a thermocouple. However, there is an uncertainty of about 1° for the absolute value of the lowest temperatures.

Cumylcaesium used throughout as initiator was prepared according to the method described earlier [8] but slightly modified. To avoid longer times of contact of the initiator with the metallic caesium, its reaction with freshly distilled cumylmethylether in THF at 30° was stopped after 5–10 min by cooling the reaction solution to −78° and immediately filtering it from the residual alkali metal and the formed caesium-methoxide. Since only 10–20 per cent of the added cumylmethylether could react within the short reaction time, the remaining cumylmethylether in the initiator solution was removed by distillation to dryness at low temperature, and the initiator redissolved in pure THF just before it was used.

$Cs(BPh_3CN)$ was prepared and purified as described earlier [2, 18] and checked for traces of sodium. It has at 20° a dissociation constant of 9·7 × 10^{-7} mole/l [18, 19] comparable to that of $Cs(BPh_4)$, but has the advantage of a higher solubility in ethereal solvents.

III. RESULTS

The kinetic behaviour of (one-ended) polystyrylcaesium was studied at 25° in somewhat more detail. The results of the experiments in absence of a common ion are listed in Table 1 and shown in Fig. 1, plotted in the conventional way according to the equation

$$\bar{k}_p = \bar{k}_{p(\pm)} + k_{p(-)}(K_D/c^*)^{-1/2}. \qquad (1)$$

where $\bar{k}_p$ is the experimentally observed overall rate constant, $\bar{k}_{p(\pm)}$ and $k_{p(-)}$ the rate constants for the ion pairs and for the free anion; K_D denotes the (overall) dissociation constant and c^* the concentration of the active centres.

The straight line in Fig. 1 which may be drawn through the experimental points, yields as intercept the ion pair rate constant, $\bar{k}_{p(\pm)} = 130$ l/mole/sec, and as slope the product, $k_{p(-)}K_D^{1/2} = 3{\cdot}0_5$ $(\text{l/mole})^{1/2}$/sec, from which the dissociation constant can be estimated.

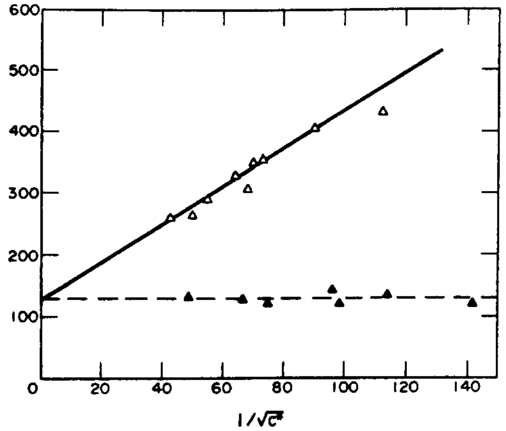

Fig. 1. The experimentally observed rate constant $\bar{k}_p$ of polystyrylcaesium at 25° in THF in absence of and in presence of an excess of the common ion salt $Cs(BPh_3CN)$ plotted vs $c^{*-1/2}$ according to Eqn. (1).

Taking $k_{p(-)}$ as 1·35 × 10^5 l/mole/sec as determined at 25° in several solvents [4,.6, 16], one obtains for the dissociation constant K_D of polystyrylcaesium in THF 5·1 × 10^{-10} mole/l.

These results deviate quite considerably from those of earlier investigations [8, 9] where the following values had been reported for the same temperature: $\bar{k}_{p(\pm)} = 20$–25 l/mole/sec, $k_{p(-)}K_D^{1/2} = 4{\cdot}2$ $(\text{l/mole})^{1/2}$/sec, and $K_D = 4{\cdot}7 \times 10^{-9}$ mole/l as determined by conductance measurements. Similar discrepancies had already earlier been found and discussed [5, 6] concerning results for polystyrylsodium in THF [20, 21] and DME [22].

The observed deviation concerning $k_{p(-)}K_D^{1/2}$ may not be considered as critical because due to the small dissociation constant of polystyrylcaesium, both kinetic and conductometric experiments are greatly affected by dissociating decomposition products leading to decreased values for $\bar{k}_p$ and to higher values for K_D. From the quoted value [8] for the product $k_{p(-)}K_D^{1/2}$, one obtains with the above value for $k_{p(-)}$ a dissociation constant of 9·7 × 10^{-10} mole/l differing by a factor of 2 only; this is not larger than the probable error of the measurements.

The large deviation observed for the ion pair rate constant $\bar{k}_{p(\pm)}$ mainly arises from the uncertain extrapolation of $\bar{k}_p$ according to Eqn. (1). Therefore, a series of experiments was performed at 25° in the presence of

Table 1. Kinetic results for polystyrylcaesium in THF at 25° in presence of and in absence of a common ion

No salt addition		Addition of excess of $Cs(BPh_3CN)$		
$c^* \times 10^4$ (mole/l)	$\bar{k}_p$ (l/mole/sec)	$c^* \times 10^4$ (mole/l)	$c^* \times 10^{+3}$ Salt (mole/l)	$\bar{k}_{p(\pm)}$ (l/mole/sec)
5·06	260	4·2	1·0	129
4·04	264	3·29	1·0	120
3·33	292	2·25*	0·8	128
2·43	330	1·78*	1·2	120
2·15	301	1·09*	0·5	143
2·02	350	1·03	0·5	121
1·89	354	0·77	7·5	135
1·22	403	0·51	7·5	123
0·79	435	—	—	—

* Aged initiator.

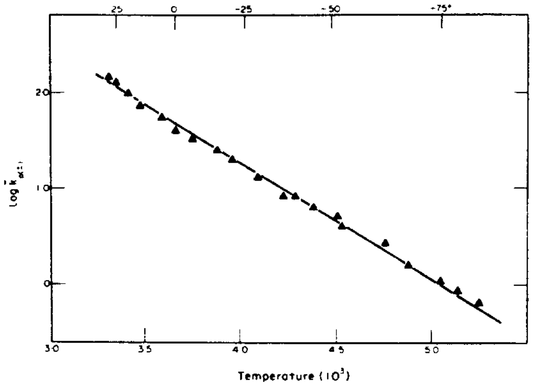

Fig. 2. Arrhenius plot for the ion pair rate constant $\bar{k}_{p(\pm)}$ of polystyrylcaesium in THF.

various concentrations of the common ion salt, Cs(BPh$_3$CN). The ratio, [Cs(BPh$_3$CN)]/c^* was varied between 2·5 and 150. The results, summarized in Table 1 and shown in Fig. 1 (dashed line), confirm the ion pair rate constant to be 130 l/mole/sec. There is no discernible trend of the observed rate constant with the varying salt concentration, an indication that the dissociation of the active centres is completely suppressed and that no triple ions are formed.

The ion pair rate constant $\bar{k}_{p(\pm)}$ was measured over a wider range of temperature in the presence of about 1–2 × 10^{-3} mole/l Cs(BPh$_3$CN). The results are shown in Fig. 2 in an Arrhenius plot. The slight curvature exhibited by the line as drawn in Fig. 2 may not be significant because of the uncertainty for the absolute values of the lowest temperatures. Assuming a straight line, one obtains a frequency factor of 1·2 × 10^6 and an activation energy of 5·53 kcal/mole. Szwarc *et al.* [8] reported similar values viz. 2·2 × 10^5 for the frequency factor and 5·7 kcal/mole for the activation energy.

IV. DISCUSSION

The results obtained here for the ion pair rate constant $\bar{k}_{p(\pm)}$ settle the inconsistency mentioned above in that $\bar{k}_{p(\pm)}$ determined in the series of solvents DME (150) [7], THF (130), THP (50) [11] and DO (22) [10] as indicated in parentheses and in l/mole/sec for 25°, follows the trend of decreasing solvation ability of the solvent. A similar trend has been observed with other anionic polymerization systems [5, 6, 23].

However, a relatively small frequency exponent $A_{(\pm)}$ of 6·0$_5$ has been found again. Originally, it was hoped

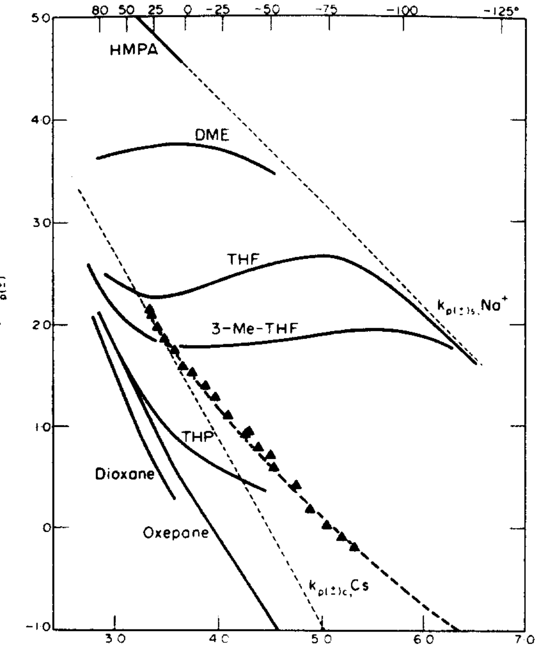

Fig. 3. Arrhenius plot for the ion pair rate constant $\bar{k}_{p(\pm)}$ for polystyrylsodium in various polar solvents (drawn lines, solvent as indicated, HPMA = hexamethyl phosphoricacid-triamide) and for polystyrylcaesium in THF (▲). The dashed line is computed according to Eqn. (2). (See text.)

that the Arrhenius line for $\bar{k}_{p(\pm)}$ as shown in Fig. 2 might exhibit a curvature sufficiently significant to permit a straightforward explanation in terms of contact and solvent separated ion pairs [24]. Such an interpretation has already been suggested, but was finally rejected by Szwarc *et al.* [8].

In the meantime, more pertinent kinetic data has been evaluated, in particular, for polystyrylsodium. The consistency of these results encourage a re-examination of this problem. For that purpose, Fig. 3 shows in an Arrhenius plot the temperature behaviour of the (overall) rate constant $\bar{k}_{p(\pm)}$ of the polystyrylsodium ion pairs as lines for all solvents investigated together with the experimental results for the polystyrylcaesium ion pairs in THF.

The kinetics for polystyrylsodium has been detailed in several papers [6, 15, 16]; they may be summarized thus.

The overall rate constant $\bar{k}_{p(\pm)}$ is composed of two additive terms reflecting the contribution of the contact ion pair and the solvent separated ion pair to the

Table 2. The thermodynamic parameters and the Arrhenius parameters for the rate constants $k_{p(\pm)c}$ and $k_{p(\pm)s}$ of the contact and solvent separated ion pairs of polystyrylsodium in various polar solvents [15]

Solvent	$A_{(\pm)c}$	$E_{(\pm)c}$ (kcal/mole)	$A_{(\pm)s}$	$E_{(\pm)s}$ (kcal/mole)	ΔH_{cs} (kcal/mole)	ΔS_{cs} (e.u.)
DME	7·8	9·2	7·8	4·2	−5·5	−22
THF	7·8	8·6	8·3	4·7	−6·5	−34
3-Me-THF	8·0	9·2	8·3	4·4	−5·1	−32
THP	8·2	9·7	8·4	4·5	−3	−28
Oxepane	8·2	9·8	8·2*	4·5*	−1	−26
DO	8·4	10·5	—	—	—	—

* Assumed in the calculation of the thermodynamic parameters.

polymerization, and therefore, is described by the equation

$$\bar{k}_{p(\pm)} = k_{p(\pm)c} + k_{p(\pm)s}\frac{K_{cs}}{(1+K_{cs})}, \tag{2}$$

where $k_{p(\pm)c}$ and $k_{p(\pm)s}$ are the individual rate constants and K_{cs} is the equilibrium constant for the two types of ion pairs.

Considering the temperature dependency of these constants, all drawn curved lines in Fig. 3 can be quantitatively described by Eqn. (2) using the data for the Arrhenius parameters and the thermodynamic parameters as listed in Table 2.

As one can see from Table 2, the frequency exponents $A_{(\pm)c}$ and $A_{(\pm)s}$ are both very close to an average value of 8·0 also found for $A_{(-)}$, the frequency exponent of the rate constant $k_{(-)}$ for the free polystyrylanion, regardless of the solvation ability of the solvent and regardless of the distance of separation of the electric charges. Moreover, this value can be considered as "normal" [25], since it lies in the range predicted by Eyring's theory on account of the corresponding polymerization entropy [26].* This must be considered as proof that the transition state for monomer addition is basically the same with all differently reactive species of polystyrylsodium. In particular, the value of $A_{(\pm)c}$ reveals that the monomer addition to the contact ion pair does not occur via an insertion reaction because then the frequency exponent, and also presumably the activation energy, would be expected to be considerably decreased.† Furthermore, $A_{(\pm)s}$ shows that the bulkiness of the solvated gegenion in the solvent separated ion pair does not cause any significant steric hindrance in the propagation step which would also result in a decrease of the frequency factor.

Therefore, the frequency factor found for $\bar{k}_{p(\pm)}$ of polystyrylcaesium ion pairs can hardly be explained either as due to an insertion reaction or to be steric in origin. Thus $\bar{k}_{p(\pm)}$ is unlikely to be the rate constant of one type of ion pairs, viz. that of the contact ion pair. It seems to be more plausible to also describe $\bar{k}_{p(\pm)}$ by Eqn. (2), i.e. to assume a kinetically relevant contribution of the solvent separated ion pair to the polymerization resulting in a decrease of $A_{(\pm)}$ for a certain temperature range [24].

It may be argued that the existence of solvent separated ion pairs in polar solvents could not be established either with other dissociating caesium compounds in contrast to many sodium compounds, where the existence of two different types of ion pairs could clearly be shown by extending conductometric [5, 27, 28, 29] and spectroscopic [12, 13, 30] measurements over a wide range of temperature. Both methods succeeded for sodium compounds because the equilibrium between the two types of ion pairs can be shifted in favour of the solvent separated ion pair by lowering the temperature to such an extent to give measurable effects. This is possible because, due to the strong solvation of the sodium ion, the transition from the contact to the solvent separated ion pair is considerably exothermic as also can be seen for example from Table 2. For the corresponding caesium compounds [5], this cannot be expected since their dissociation enthalpy amounts only to −2·0 kcal mole in the more polar solvents, a value too small to enable a considerable shift of the equilibrium within the experimentally accessible temperature range.

Despite this understandable failure of the conventional methods to prove the existence of different kinds of ion pairs for caesium compounds, it may be pointed out that, in principle, solvent separated ion pairs should always exist when contact ion pairs dissociate into free ions. This follows from kinetic considerations concerning the association process of the free cation and anion when forming the contact ion pair. The question only is whether the state where the ions are separated by one solvent molecule only can be treated as a thermodynamically distinct species which the term solvent separated ion pair implies. In the authors' opinion, this, however, can be decided only by relaxation measurements of the dissociation process: the appearance of two distinct relaxation times is a definite indication for two thermodynamically distinguishable kinds of ion pairs.

As such measurements have not yet been performed, the discussion is confined to the question whether the low frequency exponent $A_{(\pm)}$ can reasonably be explained by splitting $\bar{k}_{(\pm)}$ into two additive terms according to Eqn. (2).

For that purpose, we assume the Arrhenius parameters for the solvent separated ion pair of polystyrylcaesium to be essentially the same as with polystyrylsodium. Taking the average of the corresponding data listed in Table 2, $A_{(\pm)s}$ is supposed to be 8·1 and $E_{(\pm)s}$ to be 4·2 kcal mole. For the reasons outlined above, the frequency exponent $A_{(\pm)c}$ also is assumed to be 8·0 as suggested by the mean of the corresponding values in Table 2. With these fixed values, the thermodynamic parameters for the equilibrium constant K_{cs} and the activation energy $E_{(\pm)c}$ are varied such that the experimental points in Fig. 3 can be fitted. The dashed line in Fig. 3 fitting acceptably the experimental points was thus calculated with an activation energy $E_{(\pm)c}$ for the rate constant of the contact ion pair of 8·1 kcal/mole, an enthalpy ΔH_{cs} of −0·8 kcal/mole and an entropy difference ΔS_{cs} between the two assumed types of ion pairs of −19·5 e.u. In Fig. 3, the Arrhenius lines for the rate constants of the solvent separated ion pair and for the contact ion pair are represented as dotted straight lines. The former is identical to that for the solvent separated ion pair of polystyrylsodium.

Although this set of data is not unambiguous,‡ the computed values are in the expected range. Thus $E_{(\pm)c}$ compares well with that of 7·4 kcal/mole found for the ion pair constant of polystyrylcaesium in benzene [31], and with that for the polystyrylsodium contact ion pair in THF, which presumably has a somewhat higher activation energy. The thermodynamic parameters ΔH_{cs} and ΔS_{cs} also appear to be reasonable. They are approximately half the corresponding values for the dissociation of polystyrylcaesium in THF [8] which

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* In ref. [25], it is questioned whether such a value can be expected for ionic polymerization but, since the frequency exponents for the corresponding rate constants for the anionic polymerization of α-methylstyrene [23] also follow the prediction of this theory, this concept may be applied to ionic as well as to radical polymerization.

† For instance, the frequency exponents for the transition of the contact ion pair to the solvent separated ion pair of polystyrylsodium, which is an insertion reaction of a solvent molecule, is found to be only about 3 in THF and in THP, the corresponding activation energy to be 2·5 kcal/mole and 4–5 kcal/mole [15], respectively.

‡ Including the kinetic results reported for other solvents, which could lead to less ambiguous data, seems to be unwarranted at present because of the observed deviations.

occurs at 25 with an enthalpy of about −2·0 kcal/mole and an entropy ΔS_D of −44 e.u. The splitting of ΔS_D into two almost equal additive terms on account of a two step dissociation may be expected since the same phenomenon also is observed for the dissociation entropy of polystyrylsodium [6] and other sodium compounds in polar solvents [5, 28].

These considerations show that the existence of two types of ion pairs cannot be excluded for polystyrylcaesium in THF. Corresponding kinetic investigations in other solvents may resolve this question. It may be mentioned that for polymethylmethacrylcaesium in THF the existence of two differently reactive ion pairs had also to be postulated in order to explain results obtained from the analysis of the molecular weight distribution of polymethylmethacrylates anionically prepared with Cs^+ as gegenion [32].

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