(18) D. E. Dorman, M. Jautelat, and J. D. Roberts, *J. Org. Chem.*, **36**, 2757 (1971).
(19) K. F. Elgert, G. Quack, and B. Stutzel, *Polymer*, **16**, 154 (1975).
(20) M. A. Golub, "Polymer Chemistry of Synthetic Elastomers", Part 2, J. P. Kennedy and E. G. M. Törnquist, Eds., Interscience, New York, 1963, p 939.
(21) A. Priola, N. Passerini, M. Bruzzone, and S. Cesea, *Angew. Makromol. Chem.*, submitted.

Quantum-Chemical Study of the Reactivity in Anionic Polymerization. 1. The Effect of the Polarity of Medium and Alkali Metal Cations on the Rate of Propagation Reaction

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ABSTRACT: The effect of counterion and solvent polarity on the activation energy of the propagation reaction of styrene anionic polymerization has been studied by a semiempirical quantum-chemical method. The structures of ion pairs of the polymer anion with cation and of the activated complex have been estimated. The effects of solvent polarity and of various counterions on these structures have been investigated and changes in activation energies evaluated. The theoretical properties found are in qualitative agreement with the experimental data available.

Much attention has recently been devoted to processes taking place during anionic polymerization.[1-5] Research carried out in this field led to the conclusion that the reactivity (either in initiation or in propagation reactions) is markedly affected by ion-pair formation between reacting anions and present cations. During the propagation reaction, a living polymer anion may form ion pairs with the present cations, usually alkali metal cations. Ion pairs compared with free living anions show different reactivity with respect to monomer. This has been confirmed by observations that the rate of the propagation reaction of styrene polymerization is influenced by the quality of counterion and solvent polarity (see review by Szwarc[3]). However, the detailed structure of the individual species is not known. The purpose of this paper is to study the above-mentioned effects, i.e., the effect of the quality of counterion and the effect of solvent polarity, on the activation energy of the propagation reaction from the theoretical point of view. The semiempirical quantum-chemical calculations of model structures in the propagation reaction of styrene show the possibilities of applying the theoretical methods aiming at acquiring further knowledge on the mechanism of the propagation reaction of ionic polymerization.

Calculations

In the quantum-chemical study of the propagation reaction of anionic polymerization two problems have to be overcome: (i) choosing the proper quantum-chemical method able to well define the ion-pair formation between anion and alkali metal cation and the solvent effect; and (ii) choosing a simple model of the initial state and activated complex because the polystyrene anion reacting with the monomer of styrene in the presence of cations in polar medium represents a very complicated system in view of the quantum-chemical calculation.

As to the first problem, in calculations of the systems similar to those considered here, current all-valence methods fail.[6,7] The Pariser–Parr–Pople method in π approximation has recently been modified by us;[8] the method enables consideration of alkali metals. Since the method was successfully applied to the study of ion pairs between radical anions and cations,[9] we have used it also in the present paper. All details concerning this method have been described previously.[8,9]

A simplified model system was chosen (Figure 1) to evaluate theoretically the effect of counterion and solvent in the propagation of anionic polymerization. The activated complex was considered as a symmetrical system, where $r_{C_1-C_2} = r_{C_2-C_3} = 1.53 \times 10^{-10}$ m and the position of the cation Me$^+$ varied according to the axis of symmetry in the plane of complex corresponding to the model proposed by Szwarc.[1] We did not take account of the activated complex proposed by Szwarc later[3] since the energy of the asymmetrical complex was higher than that of the symmetrical one. Calculations centered mainly on evaluating the interaction of alkali metal. Therefore in the structures shown in Figure 1 we changed the position of cations in the directions outlined and looked for the energetically most stable structure. The distance r_{Me} varied between 1.5×10^{-10} and 6.5×10^{-10} m.

The stability of the individual structures is influenced not only by the electronic structure itself but also by the solvation energy. Regarding the charged systems under study the decisive solute–solvent interaction will likely be of electrostatic character. This part of the solvation energy can be expressed by the relation,[10]

$$E_{\text{solv}} = -\tfrac{1}{2}\sum_{\mu}\sum_{\nu} Q_\mu Q_\nu \gamma_{\mu\nu}\left(1 - \frac{1}{\epsilon}\right) \tag{1}$$

where Q_u and Q_ν are the net charges on the atoms μ and ν of solute molecule, calculated by quantum-chemical method, $\gamma_{\mu\nu}$ is the electron-repulsion integral, and ϵ is the dielectric constant of the medium.

By adding E_{solv} to the total energy of the system of ion pair or activated complex, we obtain the summary energy describing the energetic state of the system in solvent.

Results and Discussion

Figure 2a shows the results of calculations of the total energy for ion pair (initial state) without solvation energy as a function of r_{Me} and Figure 3a shows the results for the activated complex.

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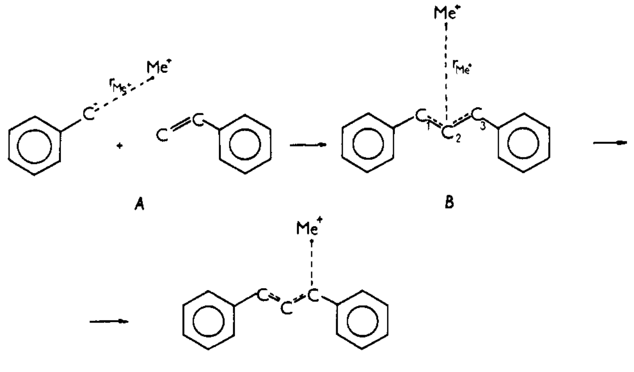

Figure 1. Model structures considered in the calculation of the activation energy: A, initial state; B, activated complex.

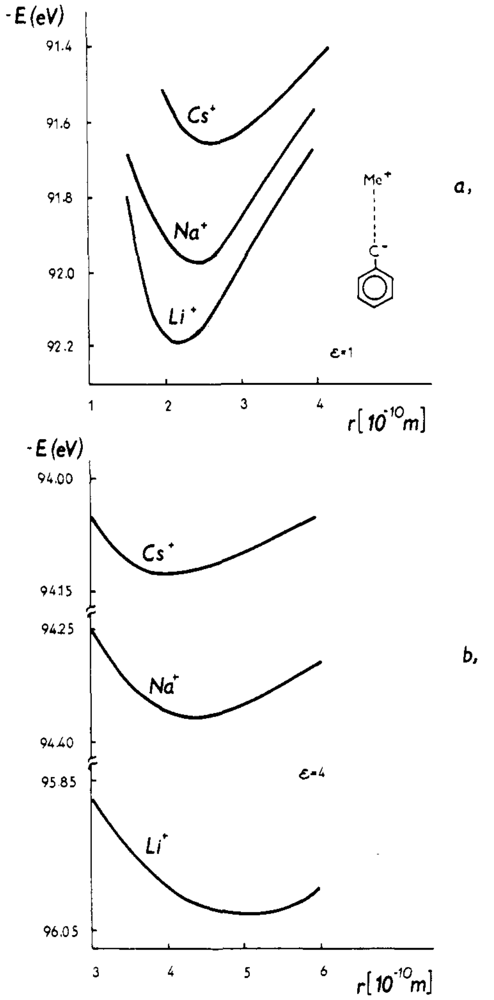

Figure 2. A plot of the total energy of the system of the initial state vs. the distance of Me^+ from the benzyl anion: (a) without consideration of solvation energy ($\epsilon = 1$); (b) including solvation energy ($\epsilon = 4$).

The summary energy of the styrene system (total electron energy + solvation energy) for the dielectric constant $\epsilon = 4$ for ion pair and activated complex is presented in Figures 2b and 3b.

Pronounced minima were obtained on the curves of the total energy corresponding to the most stable structures by calculations of all structures. If the effect of the solvation energy is not considered, the most stable structure of ion pairs is for the distance of alkali metal cation between 2.2×10^{-10} and 2.6×10^{-10} m. With increasing radius of cation (from Li to Cs) the minimum shifts to greater distances and the stability of the ion pair decreases, which is in line with the intuitive ideas about the structure of ion pairs.

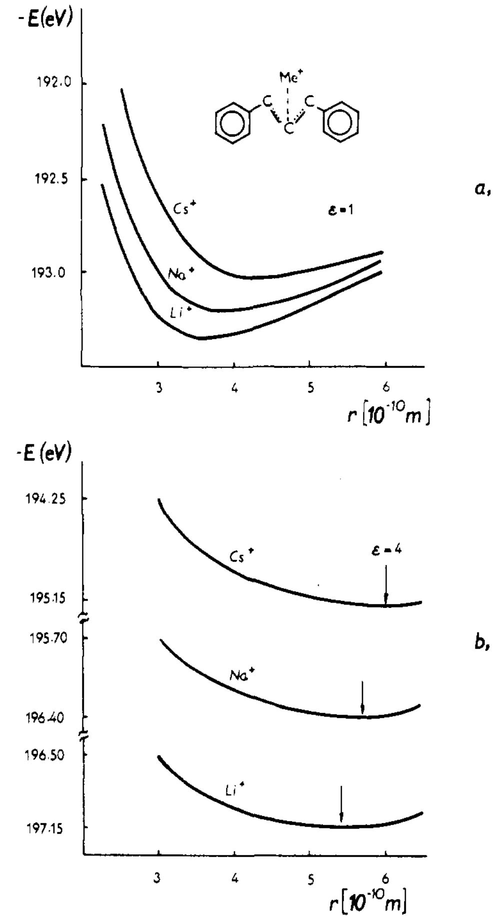

Figure 3. A plot of the total energy of the system of the activated complex vs. the distance of Me^+ from C_2: (a) without consideration of solvation energy ($\epsilon = 1$); (b) including solvation energy ($\epsilon = 4$).

Table I
Solvation Energy and Equilibrium Distance of Cation in Ion Pairs

Me^+	$-E_{solv}$, eV	$r_{Me} \times 10^{-10}$ m
Li^+	4.58	2.25
Na^+	4.15	2.50
Cs^+	2.94	2.50

For the considered distances only a very small amount of electron density is transferred from anion back to alkali metal cation (0.02–0.07 e), i.e., the whole supersystem corresponds in principle to the structure $C_7H_7^-Me^+$. For such a supersystem, solvation energy expressed according to relation 1 assumes considerable values. Table I gives the values for solvation energy (for $\epsilon \rightarrow \infty$) for ion pairs in the most stable configuration without considering solvation energy.

It is seen that the solvation energy for ion pairs decreases from Li to Cs. As is evident from relation 1, with the increasing distance of cation, the solvation energy monotonously increases since the main repulsion term $-{}^1/_2(1 - 1/\epsilon)\sum_{\mu\neq Me^+} Q_\mu Q_{Me^+}\gamma_{\mu Me^+}$ monotonously decreases, while the attraction terms are almost the same. This results in a shift of the minima of the summary energy with the increasing solvation (with the increasing dielectric constant) to greater distances r_{Me}. Figure 2b shows that this effect is largest for ion pair with Li and decreases in the direction toward Cs.

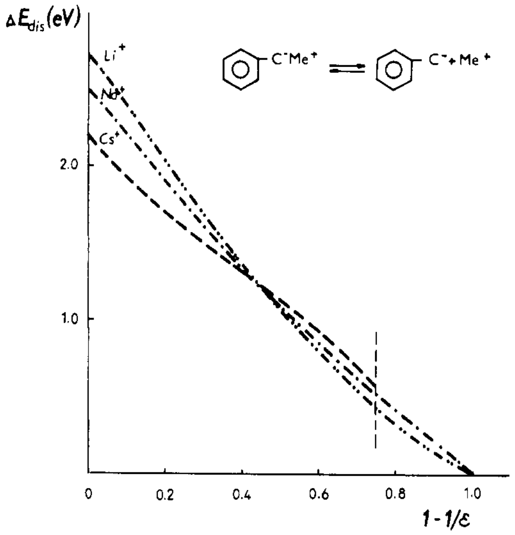

Figure 4. Changes in the dissociation energy of the ion pair of benzyl anion with individual cations as a function of ϵ.

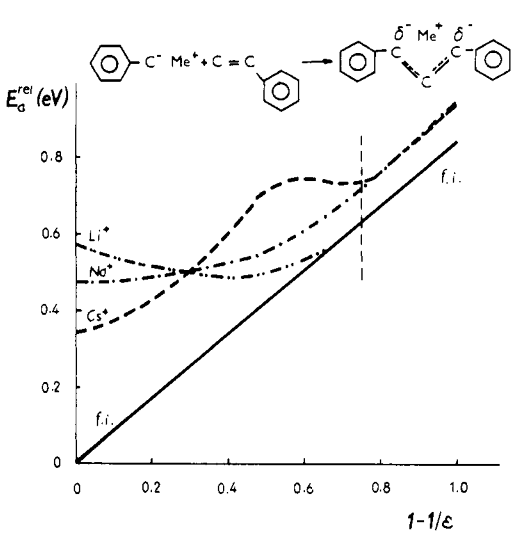

Figure 5. A plot of the relative activation energy E_a^{rel} of the propagation reaction vs. ϵ for free ions (f.i.) and varions cations participating in the reaction.

In the ion pair with Li the solvation energy is so large that from a certain value of dielectric constant ($\epsilon \geq 6$) the minimum of the summary energy showing a tendency to decrease is not obtained for the values of r_{Li} considered. This result corresponds to a "decay" of ion pair so that only free dissociated ions are present in very polar media.

Calculation of the difference in energies, ΔE_{dis}, will illustrate dissociation of ion pairs considered.

$$E_{dis} = E_{T,benzyl\,anion} + E_{solv,benzyl\,anion} + E_{solv,Me^+} - E_{T,ion\,pair} - E_{solv,ion\,pair}$$

Figure 4 shows ΔE_{dis} thus calculated for individual ion pairs as a function of ϵ. It is seen that in weakly polar media $(1 - (1/\epsilon)) < 0.4$ the most dissociated ion pairs are those with Cs, less with Na, and least with Li. In polar media these ratios reverse and for very polar medium, in the case of Li ion pairs, "decay" as has been mentioned above.

An analogous method was employed for studying the activated complex where the position of alkali metal varied (Figure 3). The curves represent sections through potential hypersurface passing through the saddle point (in terms of the proposed model for activated complex). The dependence of the total energy on the distance r_{Me} yields the energy minima for the distance 3.5–4.5×10^{-10} m; the change of counterion leads to the effects similar to those for ion pairs (in the initial state). The solvation effect (for large ϵ) leads in all cases to separation of alkali metal from the activated complex. The result indicates that in very polar medium, the alkali metal cation should not participate in the formation of the activated complex.

Simultaneous evaluation of both states, A and B, i.e., ion pair in the initial state and activated complex, provides information on activation energy. The activation energy of the process investigated may be calculated from the summary energies for individual components as follows:

$$E_a = E_{activated\,complex} - E_{ion\,pair} - E_{styrene}$$

Therefore we had to calculate also the summary energy for styrene:

$$E_{styrene} = E_T + E_{solv} = -101.0254 + (-0.0075) = -101.0329 \text{ eV}$$

If the alkali metal cation does not take part in the reaction, the activation energy E_a can be computed for free ions. Figure 5 shows the curves of the activation energies thus obtained as a function of the dielectric constant ϵ of solvent.

With regard to the approximativeness of the method, we did not aim at interpreting the numerical values of activation energies for these reactions but at evaluating relative changes of E_a caused by a change in the alkali metal or a change in the solvent polarity. Therefore Figure 5 presents relative values for activation energies E_a^{rel} (related to E_a for free ions without solvation energy). As is evident from Figure 5, the activation energy will increase generally with increasing solvent polarity. This is due to the fact that the solvation stabilization is for the initial state, i.e., for ion pairs, greater than in the activated complex. Delocalization of the negative charge is greater in the π system of the activated complex than in the π system of the initial state, the solvation energy of the "anion part" being larger for a smaller anion.

It is interesting that in the propagation reaction in the presence of Li the activation energy dependent on dielectric constant has a minimum. It is probably connected with the fact that in this region of solvent polarity it is the activated complex that is better stabilized by Li^+ compared with ion pair.

The propagation reaction through free ions has for any value of the dielectric constant lower activation energy than the corresponding reactions of ion pairs. This agrees with experimental findings.[3] Further interesting knowledge can be achieved from the dependence mentioned above. Over the range of weakly polar media $[(1 - (1/\epsilon)) < 0.3]$, the activation energy decreases and the reactivity of ion pairs increases in the order Li < Na < Cs. On the contrary, in medium polar solvents the order of the values for E_a^{rel} changes: Li > Na > Cs. With respect to the simplicity of the model and the calculation method employed, qualitative agreement between these theoretical conclusions and the rate constants determined experimentally for styrene propagation with various cations in dioxane and tetrahydrofuran is encouraging.

It was found experimentally that in a less polar solvent (dioxane) the reactivity of the system polystyrene anion in the presence of a counterion of the alkali metal with Li^+ is lowest, greater with Na^+, and greatest with Cs^+. The reverse order of the reactivity was found in tetrahydrofuran. Agreement between the calculated and experimental order for less polar solvent will be achieved if in our approximative model the solvent polarity of medium is $(1 - (1/\epsilon)) \leq 0.3$; for a more polar medium agreement will be attained when $(1 - (1/\epsilon)) = 0.3$–0.6. Naturally, in

Table II
Rate Constants for Propagation Reaction of Anionic Polymerization of Styrene at 25 °C

counterion	k_{ap}, L mol^{-1} s^{-1}	
	dioxane	tetrahydrofuran
Li$^+$	0.94[a]	160[c]
Na$^+$	3.4[a]	80[d]
Cs$^+$	15[b]	22[c,d]

[a] Reference 11. [b] Reference 12. [c] Reference 13. [d] Reference 14.

the extremely simplified model postulated in the present paper one cannot expect quantitative accord between the dielectric constants of solvents used in experiment and the dielectric constant from the theoretical model.

Table II indicates that by transfer from dioxane to tetrahydrofuran at constant counterion (both for Li$^+$ and Na$^+$) the rate constant increases markedly and for Cs$^+$ it changes slightly. In order to explain this phenomenon and for more complex evaluation of the problem, account has to be taken of the fact that as the solvent polarity increases, dissociation of ion pairs into free ions increases (Figure 4); these free ions are more reactive. This means that the reactivities of free ions, ion pairs, and their dissociation equilibrium have to be considered as they are expressed by relation for the rate constant k_p[1].

$$k_p = k_\pm + (k_- - k_\pm)K_{diss}^{1/2}LP^{-1/2}$$

where $k_\pm$ is the rate constant for propagation reaction of ion pairs, k_- is the rate constant for propagation reaction of free anions, K_{diss} is the equilibrium constant for dissociation ion pairs, and LP is the concentration of living polymer.

By combining the effect of the solvent polarity on $k_\pm$ and K_{diss} the trends shown in Table II can be explained qualitatively also in our approximative model. Moreover the problem is complicated as is indicated by the fact that according to calculations another reaction path should exist in polar media where the structures forming ion pair in the initial state pass through the activated complex not containing any alkali metal.

When evaluating the theoretical results, it should be kept in mind that apart from the approximativeness of the method used for calculation and the model studied, changes in the activation entropy, which might in some cases affect considerably the total reactivity, were not considered. In spite of this, the calculations presented led to interesting findings which may be of some aid in explaining various effects on the rate and mechanism of anionic polymerization.

References and Notes

(1) M. Szwarc, "Carbanions Living Polymers and Electron Transfer Processes", Wiley-Interscience, New York, 1970.
(2) M. Szwarc, Ed., "Ions and Ion Pairs in Organic Reactions", Vol. I, Wiley-Interscience, New York, 1972.
(3) M. Szwarc, Ed., "Ions and Ion Pairs in Organic Reactions", Vol. II, Wiley-Interscience, New York, 1974.
(4) N. G. Gaylord and S. S. Dixit, *J. Polym. Sci., Macromol. Rev.*, 8, 51 (1974).
(5) N. L. Holy, *Chem. Rev.*, **74**, 243 (1974).
(6) T. A. Claxton and McWilliams, *Trans. Faraday Soc.*, **65**, 3129 (1969).
(7) S. Miertuš and O. Kysel', *Chem. Phys. Lett.*, **35**, 531 (1975).
(8) S. Miertuš, O. Kysel', and P. Mach, *Collect. Czech., Chem. Commun.*, in press.
(9) S. Miertuš, O. Kysel', and P. Mach, *Collect. Czech., Chem. Commun.*, in press.
(10) I. Jano, *C. R. Hebd. Seances Acad. Sci.*, **261**, 103 (1965).
(11) D. N. Bhattacharyya, J. Smid, and M. Szwarc, *J. Phys. Chem.*, **69**, 624 (1965).
(12) F. S. Dainton, G. C. East, G. A. Harpell, N. R. Hurworth, K. J. Ivin, R. T. LaFlair, R. H. Pallen, and K. M. Hui, *Makromol. Chem.*, **89**, 257 (1965).
(13) D. N. Bhattacharyya, C. L. Lee, J. Smid, and M. Szwarc, *J. Phys. Chem.*, **69**, 612 (1965).
(14) T. Shimomura, K. J. Tölle, J. Smid, and M. Szwarc, *J. Am. Chem. Soc.*, **89**, 796 (1967).

Quantum-Chemical Study of the Reactivity in Anionic Polymerization. 2. The Effect of Electronic Structure of Monomer on the Rate of Propagation Reaction

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ABSTRACT: The effect of a change in the structure of monomer on the activation energy of the propagation reaction of variously substituted styrene monomers with living styrene polymer has been investigated by the semiempirical quantum-chemical method. The theoretical conclusions are in qualitative agreement with the experimental data available.

In part 1 of this series,[1] interesting theoretical knowledge was acquired on the effects of various counterions and solvent polarity upon the relative activation energy of the propagation reaction of styrene by semiempirical quantum-chemical calculations, by employing a simple model of activated complex. In addition to these effects, the activation energy and thus also the rate of propagation reaction depend evidently on the electronic structure of polymerizing particles. The effect of the structure was studied experimentally for styrene copolymerization with styrene derivatives,[2] where the following can be observed: (i) the effect of the change in the structure of polymer anion during reaction with the same monomer; and (ii) the change in the reactivity of variously substituted monomers with the same living anionic end of polymer.

In the present paper we theoretically investigated propagation reactions of living styrene polymer with para-substituted styrene monomers.

Calculations

The Pariser–Parr–Pople method in the π approximation[3] was used for calculating the energies of individual systems and the activation energy of the propagation reaction. The method has already been used

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