*Macromolecules* **2001,** *34,* 1143−1147

# Articles

## Rate Constants of Cationic Polymerizations and Mayr's Rate Constants Reconciled (Developments in the Theory of Cationic Polymerization, Part XIII[†])

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*Received August 1, 2000; Revised Manuscript Received December 12, 2000*

ABSTRACT: The rate constants $k_2$ for the attack of carbenium ions on an alkene, determined by Mayr for nonpolymerizing systems, are ca. 4 orders of magnitude greater than the $k_p^+$ for the propagation of cationic polymerizations, which involve ostensibly the same reaction. This discrepancy is explained here as due to the different monomer concentrations [M] used in the two types of experiment. The argument starts from the fact that the planar, trigonal carbenium ion has two principal complexing sites, one on each side of the ion. These positions are competed for by all the constituents of the reaction mixture, which include the monomer, and therefore the characteristics of the ion are determined by the nature of its solvators. At high [M], the carbenium ions are predominantly solvated by the monomer, and they are less reactive than those complexed by the polar, but bulky solvent when [M] is low. The reason is that solvation by the $\pi$-donor monomer on both sides reduces the charge density at the carbenium ion so much that the covalent bond formation to monomer, the propagation, requires a considerable activation energy. However, solvation by the solvent has a so much smaller effect on the charge density at the $C^+$ atom, that the cation solvated only by solvent can polarize the incoming monomer sufficiently for the mutual potential energy between ion and molecule to lead to bond formation with little activation energy. Therefore, since the [M] in Mayr's experiments are smaller than those in the polymerizations, the cations in the two types of experiments are essentially different species, and therefore their kinetic constants are different. Mayr's rate constants are essentially the propagation rate constants extrapolated to $[M] = 0$, and they are likely to be all very similar for the same classes of monomers. The long quest for the "real" $k_p^+$ has therefore been ended and the meaning of the $k_p^+$ values selected by the present author has been established.

### 1. The Problem

This paper is concerned with the resolution of a discrepancy between a set of kinetic constants for cationic polymerizations selected by the present author as the most reliable recorded in the literature[1] and the rate constants for ostensibly similar reactions measured by Mayr, who has emphasized the urgent need to resolve the disagreement.[2] No other adequate theoretical attempts to do so are known to this author.

**1.1. Preamble.** The rate constants $k_p^+$ for the propagation of cationic polymerizations were long believed to be single quantities characteristic for each monomer which could be defined precisely and unambiguously, like those of other types of polymerization. Then the present author showed that in any cationic polymerization there might be more than one species propagating the reaction, from which it follows that the nature and relative proportions of the different chain-carriers must depend on the physicochemical circumstances prevailing during the reaction, and that therefore the measured rate constants may be composite,[1,3,4] and for that reason cannot properly be called "constants". Moreover, the relative concentration of the different kinds of chain carriers must change during the lifetime of the polymerization, in any case because of the consumption of the monomer, and possibly also for other reasons. Such polymerizations, in which more than one species consumes the monomer, were termed "enieidic".[3−5] Among the possible propagators present simultaneously in a polymerizing solution, he recognized that the solvation by solvent and by monomer would produce distinct species of cations, each of which could be unpaired or paired, and the differently solvated cations would have different $k_p^+$ and $k_p^\pm$ and the ion pairs would have different dissociation constants $K_D$. As a result of his detailed analysis of most of the relevant claims, he compiled a list of what he regarded as reliable rate constants $k_p^+$ for the attack on an alkenic monomer molecule by an unpaired carbenium ion, solvated mainly by the monomer which is being polymerized.[1]

At about the same time, Mayr measured the rate of attack of various types of carbenium ions on alkenes by new and ingenious methods. His rate constants $k_2$ for tertiary carbenium ions are ca. 4 orders of magnitude greater than the $k_p^+$ values recommended by this author.[1] Despite detailed discussions between Mayr and the present writer, involving also a detailed examination of Mayr's methods, a reason for the discrepancy could

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[†] Plesch, P. H. Part XII. *Eur. Polym. J.* **1993**, *29*, 121−124.

10.1021/ma0013509 CCC: $20.00

not be discovered in the mid-1990s.[2] The purpose of the present paper is to suggest one, and thus to explain the discrepancy.

**1.2. Summary of Mayr's Findings.** Mayr's work had shown that several features which could have been responsible for the discrepancy in fact only had minor effects on the order of magnitude of his rate constants, $k_2$, which are close to that of binary collisions, i.e., ca. $10^9$ L mol$^{-1}$ s$^{-1}$. The findings for secondary and tertiary carbenium ions were very similar. Mayr found $k_2$ to be almost independent (i.e., changed by less than a factor of ca. 4) of the length of the molecule carrying the charge or of the chain attached to the double bond. Also, the $k_2$ were not much affected by a change of solvent from hexane to $CH_2Cl_2$. Therefore there seemed to be few variables left that could be responsible for the discrepancy.

## 2. The Solution

**2.1. Origin of the Discrepancy.** We need to reexamine the basic assumptions underlying the interpretation of the reaction under discussion, which is the attack of an organic cation $R^+$ on an alkene, M, to give another cation, $RM^+$:

$$R^+ + M \rightarrow RM^+$$

Its rate constant $k_2$ is therefore defined by the following equation

$$\text{observed rate} = k_2[\text{alkene}][\text{attacking ion}]$$

To explain the fact that in different types of experiments very different rate constants were found for ostensibly the same reaction, we have (at least) the following options: (1) The observed rates are not those of the same processes. (2) The alkene is not the same species. (3) The concentration of the attacking ion is not what one thinks it is, either (a) because in one or the other type of experiment the measured quantity is not equal to the concentration of the ions or (b) because in fact the attacking ions are not the same species in the two types of experiment.

Options 1 and 2 can be dismissed as highly unlikely. Option 3a can be set aside just because the $k_p{}^+$ in question which should be, but are not, the same as the $k_2$, were selected as those (very few) which had been derived from reactions for which the concentration of propagating carbenium ions was deemed to have been well established and which were clearly first order with respect to the monomer.

The much-quoted rate constants for radiation-induced polymerizations of bulk monomers, which are internally of zero order, were not included (see Plesch[1] for details).

This leaves option 3b to be scrutinized closely. When the present writer did this, he realized that his puzzlement had arisen because he like others, had fallen into the trap of which he had frequently warned his students and which he has emphasized in his writings: It is a serious error to attempt to understand electrochemical phenomena by thinking of ions in isolation, because this puts them putatively into a vacuum. But the ions of concern to us do not exist in a vacuum. Ions would not leave their positions of low energy in a crystal lattice to go into solution or be formed from neutral molecules by the transfer of a charged fragment from one molecule to another if those processes were not made exoenergetic by the interaction of the ions with polar or polarizable species in their environment, most commonly the solvent. For that reason, one should always think, and indeed talk, about an ion-in-solution. The properties of an ion, including its reactivity, depend critically upon the nature of its solvation shell.[6] We can make an apt comparison with humans: When people are naked, their attributes and capabilities are very similar, but these are very different when a person is wearing a wet suit, a space-suit, or a ball gown.

The discrepancy with which we are concerned arises from assuming that the active species, i.e., the carbenium ions, are the same in Mayr's work as those which propagate the polymerizations. The message here is that they are not. The main source of the difference is the solvation of the carbenium ions by the monomer. This phenomenon has been mentioned by this writer in many of his publications from the late 1960s onward[3,7−9] and by others, and it soon became a generally accepted part of the theory of cationic polymerizations.[10] The ideas involved were given precision and elaborated,[11] and they were used to explain in detail and for the first time the phenomenology of the polymerizations initiated by ionizing radiations.[12] It will be shown here that they have a further application in explaining the mystery of the rate constants, i.e., that the reason for the discrepancy lies in the complexing of the monomer with the carbenium ion.

**2.2. Cation−Monomer Complex.** Although, as has been pointed out, many authors adopted the idea that the carbenium ions can be solvated by monomer, no one before the present author has attempted to explain why in certain situations a monomer molecule could form a stable complex with the carbenium ion instead of reacting with it.[12] In other words, the conditions under which a monomer molecule can act as a solvator to a carbenium ion instead of reacting with it have not been explained hitherto. From a different point of view, we need to find out what it is that may inhibit the addition of such a cation to an alkene when they first meet.

Our starting point is that for two naked ions of opposite charge the mutual potential energy decreases as they approach each other until a bond or an ion pair is formed or an electron or a proton is transferred and the assembly becomes stable, and the same holds for an encounter of a naked ion with a reactive molecule, such as an alkene, which is polarized by the approaching cation. For any one of these possible events not to take place, the ion needs to be *not* naked; in other words, its electrical potential must be reduced by a dispersal or attenuation of the charge. Consider first the tertiary carbenium ions, such as those derived from isobutene which, in the absence of any steric constraints, are trigonal and planar. These have two positions of minimum potential energy, one on each side of the plane. These are the sites for an anion or for the negative end of a dipole or for an $n$- or a $\pi$-donor monomer. However, as soon as one of these positions is occupied, the resulting electrical distortion weakens the electrical potential on the other side; put another way, when there is an ion or a dipole on each side of the carbenium ion, each one is held less strongly, or sits in a shallower potential trough, than if it were the only one. This simple model served well to explain hitherto unexplained features of the polymerizations by ionizing radiations,[12] and it will help us to resolve the mystery of the rate constants, and other puzzles as well. In particular, it enables us to resolve the question at the start of this section thus: In any solution of interest in the present context, there are several species competing for the prime solvation sites, the positions of minimum potential energy on either side of the cation. These competitors include the solvent, the monomer, and anions of various kinds and possibly metal halides. The success of these competitors, that is, the proportion of the complexing sites occupied by each one of the competing species, depends on their concentration through the Law of Mass Action. The equilibrium constants for the complexations are determined by the standard free energy $\Delta G°$ of the relevant interaction; this in turn is governed by the steric constraints and by the effective electrostatic attraction, which is the resultant of the charge or dipole moment and the polarizability of all the species involved. From these considerations, we conclude that if the carbenium ion is strongly complexed on one side, e.g., by being paired with an anion, then the residual positive charge on the side opposite to that occupied by the strong complexor is not strong enough to polarize the approaching double-bond sufficiently to produce the monotonically decreasing mutual potential energy which is needed for bond formation to take place without (or with a very low) activation energy. Therefore the monomer molecule settles in a potential well and is a $\pi$-donor−solvator if it is an alkene and an $n$-donor−solvator if it contains a heteroatom, such as O or N.

**2.3. Propagation.** The ternary complex consisting of the carbenium ion with an anion and a monomer molecule can isomerize with incorporation of the previously complexed monomer molecule into the chain and a shift of the positive charge to the new chain end. This is a unimolecular propagation reaction of zero order with respect to the monomer concentration. It occurs in polymerizations of bulk monomer and in nonpolar solvents, and at relatively high monomer concentrations in polar solvents.

It is appropriate to point out here just why it is not valid to assume (as is commonly done) that throughout the propagation step a paired cation will remain paired and that the resulting newly formed carbenium ion will therefore start its life paired (see, e.g., Mayr et al.[13]). On the contrary, if we follow the assumption made by the founders of Transition State Theory that the transition state can be treated as a thermodynamically stable species, it follows that because in the transition state the positive charge is less concentrated than in the ground state and because therefore the Coulombic force holding the anion is less than in the ground state, the (quasi-) dissociation constant of an ion pair of which the cation is in the transition state must be greater than the dissociation constant of an ion pair whose cation is in the ground state. Therefore the probability of the newly formed cation being paired is less than that for a cation which is in the ground state.

Any carbenium ions which are not paired have both their complexation sites occupied by the most polar or polarizable species available, which can be the solvent or the monomer, according to their relative polarities, polarizabilities, and concentrations; for paired cations, the picture applies to their other, still vacant, site. Such a situation will generally prevail in nonpolar solvents because in these the concentration of paired cations is dominant. In a polar solvent, both sites at an unpaired cation can be occupied by solvent, or one by solvent and one by monomer, or both by monomer. In the radiation polymerizations, one sees clearly that as the monomer concentration is reduced from bulk monomer, the kinetics change and they eventually become first order in monomer, whatever the solvent; the critical monomer concentration at which this happens depends on the polarity of the solvent.[12]

If we now compare Mayr's experiments with those of conventional polymer chemistry, including the radiation-induced polymerizations, we find that the single greatest difference is the monomer concentration which in most of Mayr's experiments is much lower than in most conventional polymerizations. This means that in Mayr's experiments there are relatively few alkenes in the solvation shell of the carbenium ions, or put more precisely, few of the propagating carbenium ions have even one monomer molecule in their solvation shell. Hence we conclude that Mayr's $k_2$'s for the equivalent of a propagation step are so big because the displacement of the loosely held solvating solvent molecules requires only a very small activation energy, as indeed reported by Mayr. From the opposite point of view, we can see that what makes the conventional $k_p^+$ so much smaller than Mayr's $k_2$ is the energy needed to shift the firmly bound solvating monomer molecules around into the configuration of the transition state, so that the incorporation of such a monomer molecule and the relocation of a solvating monomer molecule on the newly formed cation can occur.

In his examination of the effects of monomers complexing with the propagating carbenium ions,[11] this author pointed out that the comparison of the $k_p^+$ for various monomers obtained under normal conditions would not be very informative because the relative magnitudes of the $k_p^+$ would be those of the various carbenium ions, each one solvated at least partly by its own monomer. Therefore a meaningful comparison of the $k_p^+$ could only be made between the values obtained by an extrapolation to $[M] = 0$, and it is that extrapolated value which Mayr has measured. The irony of the situation is that at the end of the long quest for the "real" $k_p^+$, these turn out to be all approximately the same, namely, the rate constants for diffusion-controlled reactions (neglecting relatively minor differences due to differences in charge density and steric hindrance in cations of different structure). I am strongly reminded of Peer Gynt's onion! When, at the center of the onion which symbolizes his life's quest, he finds − nothing, he realizes the irony and can only explain: "How witty!"

## 3. Some Consequences and Suggestions

**3.1.** A very detailed explanation of the nature of the different propagating species will be found elsewhere,[12] as well as a discussion of the factors affecting their relative abundances, as these vary with the concentration of the monomer and the nature of the solvent.

In considering the present thesis that a change of monomer concentration can bring about a 10 000-fold change of rate constant by changing the relative abundance of chain carriers of different reactivity, one must also consider the concurrent effects of the changes in the dielectric constant of the reaction medium. These can be dramatic for ionic reactions because $K_D$ depends exponentially on the dielectric constant.

For all these reasons, to clarify the subject further, it would be most useful to do conventional kinetic experiments with diminishing [M] and Mayr-type experiments with increasing [M] with the aim of obtaining an overlap of the ranges of [M] for the two types of experiment, and for fairly obvious reasons these experiments should be done in the same polar solvent at fixed dielectric constant with compensation by, say, *n*-butane.

Mayr et al. claim that they have done this experiment by increasing [M] up to 0.6 mol/L, and that the reaction was still first order in monomer and that the rate constant was unchanged. However, in ref 12 evidence is presented showing that the change of kinetic order, signaling a change in the nature of the dominant propagating species, only starts at much higher monomer concentrations. In Figures 9 and 10 of ref 12, it is seen that for the polymerization of isobutene the variation of the rate with [M] indicates that for the solvents $CS_2$, $CHCl_3$, and $CH_2Cl_2$ significant kinetic changes start around $[M] = 4$ mol/L, and the variation of the DP of the polymers with [M] indicates clearly a change of order in the region of 5−10 mol/L (Figure 15 of ref 12). It follows that the correctly designed critical experiments remain to be done.

A referee has suggested that if the gradual replacement of monomer by solvent leads to an increase in the proportion of more reactive ions, as is proposed here, then a reduction of [M] should accelerate the polymerization of isobutene. This is so, as shown in the figures of ref 12 quoted above where the rate is seen to go through a marked maximum at around 4 mol/L.

It does seem curious that no $k_p^+$'s between the extremes of ca. $10^4$ and $10^8$ L mol$^{-1}$ s$^{-1}$ have been reported for chemically initiated polymerizations. The most likely reason is the sheer technical difficulty of measuring polymerization rates for such systems with [M] in the range of 4−8 mol/L and of determining reliably the nature and the concentration of the propagating species and the ratio of unpaired to paired ions. This the more so, since nothing less than the high-vacuum techniques used by Sigwalt, Pepper, Plesch, et al.[4] which have fallen into desuetude would be required for such an enterprise.

**3.2.** The effect of monomers on the $K_D$ of ion pairs can be tested by experiments similar to those of Bos and Treloar.[15] They found that the addition of styrene to a solution of trityl$^+$ $HgCl_3^-$ increased the $K_D$. More detailed information could be obtained from analogous conductometric experiments with salts of a variety of stable cations with a variety of unreactive anions of various sizes, such as $BF_4^-$, $BCl_4^-$, $SbF_6^-$, and tetraaryl $B^-$. These salt solutions could be titrated with 2-methylbutene-1 and other alkenes and with *n*-donor monomers such as alkyl vinyl ethers and *N*-vinylcarbazole. Some guidance in this area is provided by the conductometric titration of $Et_3O^+PF_6^-$ with $Et_2O$ in $CH_2Cl_2$, which showed clearly the increase in the dissociation constant $K_D$ of that salt due to the progressive solvation of the oxonium ion by the ether.[16]

**3.3.** The author's theory which has been used here was developed in detail to explain the polymerizations by ionizing radiations of some alkyl vinyl ethers, the polymerizations of which proceed by secondary ions. Although it was shown that the theory is also perfectly serviceable for the tertiary carbenium ions considered here, it must be realized that there is a fundamental difference between these two types of carbenium ions. When one of the bonds of the carbenium ion is a C−H bond, the solvators, especially of course an ion, can get much closer to the positive center, and they are therefore correspondingly more firmly held; to which effect is added that of a smaller steric hindrance. The most researched monomer propagating by secondary cations, apart from the alkyl vinyl ethers, is, of course, styrene. Thus, Mayr's many studies with diaryl methylium cations are directly relevant to the polymerization of styrene.

This difference between secondary and tertiary carbenium ions is strictly analogous to that between tertiary and quaternary ammonium ions: the ion pairs involving the former have much lower dissociation constants.[17] It is this difference which most probably accounts also (at least partly) for the great phenomenological differences between the behaviors of styrene and isobutene. This is attested by numerous scattered papers going back to the earliest times, but a systematic and detailed comparison is to be found only in the work of this author's group on isobutene[4] and on styrene[18] in methylene chloride with initiation by $TiCl_4$ and water over a wide range of temperature.

## 4. Related Phenomena

**4.1.** Ideas very similar to those presented here were developed by Litt and Wellinghoff[19] with regard to the formation of D−A complexes and the involvement of competition of donors (D) and solvents in the solvation shell of the acceptors (A) and of the complexes. Their theory was used successfully to account for deviations from the Benesi−Hildebrand equation.[20]

**4.2.** It follows from the present argument that the ideas of the intimate and solvent-separated ion pairs, which are useful in the context of anionic polymerizations, are not relevant for cationic polymerizations. The reason is that in contrast to the carbenium ions, the carbanions are tetrahedral, the fourth "valency" being the lobe of the electron pair. Therefore, a solvent molecule can find a potential well between the anion and the cation, but there is no suitable site on the opposite side of the anion.

**4.3.** Since this manuscript was completed, Faust and his collaborators[21] have reported a $k_p^+$ of ca. $10^9$ L mol$^{-1}$ s$^{-1}$ for the polymerization of isobutene in $^{60}/_{40}$ (v/v) hexane/MeCl at −80 °C with [M] from 1 to 2.5 mol/L. This agrees with Mayr's findings as was to be expected on the basis of the present paper.

An explanatory theory has fulfilled its purpose when it has been proved inadequate and has generated a more successful successor. The present author looks forward to that development.

**Acknowledgment.** The author thanks Prof. H. Mayr and two other referees for useful criticism and suggestions.

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MA0013509