About Propagation Rate Constants in Carbocationic Polymerizations

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Summary: Published carbocationic propagation rate constants vary between 2 10^3 and 5 10^9 $L{\cdot}mol^{-1}{\cdot}s^{-1}$, e.g. for $k_p^\pm$ with styrene in CH_2Cl_2. The low values were deduced from an evaluation of $[P_n^\pm]$, the high values from competitive experiments assuming diffusion-controlled termination. Recent kinetic and spectrophotometric studies of indene living polymerization have given intermediate values (5 10^4 to 5 10^5 $L{\cdot}mol^{-1}{\cdot}sec^{-1}$). An explanation of the high values obtained by the competition method is suggested.

Introduction

The values of the absolute rate constants of propagation in carbocationic polymerizations have been a subject of discussion for a long time. For the same monomer, e.g. styrene, in the same solvent CH_2Cl_2 and at the same temperature (-80 °C), the published values of the second order $k_p^\pm$ for ion-pairs range between 2 10^3 ⁽¹⁾ and 5 10^9 $L{\cdot}mol^{-1}{\cdot}s^{-1}$ ⁽²⁾. An intermediate value of 3 10^6 $L{\cdot}mol^{-1}{\cdot}s^{-1}$ was obtained for k_p^+ in the radiation initiated polymerization of styrene in bulk at 0°C ⁽³⁾ derived from the concentration of P_n^+ deduced from conductivity data. The low k_p^+ and $k_p^\pm$ obtained in solution were deduced from $[P_n^\pm]$ obtained by spectrophotometric UV absorption ⁽¹,⁴⁾. For other monomers in CH_2Cl_2 solution, global k_p deduced from the total active centres concentration $[P_n^+]+[P_n^\pm]$ were similar with those of styrene, e.g.~10^4 $L{\cdot}mol^{-1}s^{-1}$ for isobutylvinylether ⁽⁵⁾ and p-methoxystyrene⁽⁶⁾ at 0 °C.

The most detailed review of the k_ps obtained either in bulk or in solution was done by P. H. Plesch in 1993.⁽⁷,⁸⁾ He proposed that for polymerizations initiated by radiation in bulk, propagation was not a second order reaction between carbocation and monomer, but corresponded to a unimolecular rearrangement of growing carbocations solvated by the monomer. Assuming quantitative solvation, propagation becomes first order (zero order in [M]) and could not be compared with propagation measured at low [M] in solution. In that case, he concluded that the k_p^+ in chlorinated solvents were about 1 to 2 10^4 for isobutylene⁽⁷,⁹⁾ and styrene ⁽⁷,¹⁾, as shown in table 1.

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Initiation	t °C	Styrene			Isobutylene		Isobutyl Vinyl ether		Authors
		k_p	$k_p^{\pm}$	k_p^{+}	$k_p^{\pm}$	k_p^{+}	k_p	k_p^{+}	
ClO_4H (CH_2Cl_2)	-80	5 10^3	2 10^3	2 10^4					Pepper (1973)
	-60	1.5 10^4	2.5 10^3	3 10^4					
CF_3SO_3H (CH_2Cl_2)	-10	10^5							Vairon (1992)
	-62	10^3							
$Ph_3C^+SbCl_6^-$ (CH_2Cl_2)	0						7 10^3		Sigwalt (1976)
Cl_2-Et_2AlCl (CH_3Cl)	-45					1.2 10^4			Magagnini (1977)
γ radiation in bulk	15			3.5 10^6					Williams(1967)
	0					1.5 10^8			Williams(1969)
	-78					7.5 10^7			Williams(1967)
	0							4 10^4	Hayachi (1971) Stannett (1977)
P_nCl-$TiCl_4$ (CH_2Cl_2)	-78		-		6 10^8				Mayr (1996)
P_nCl-$TiCl_4$									Faust (2000)
CH_3Cl/Hex	-80				10^9				
$CHCl_3$/CH_2Cl_2	-75		5 10^9						

Table 1. Propagation rate constants in carbocationic polymerizations (in $L{\cdot}mol^{-1}{\cdot}s^{-1}$)

More recently, very large $kp^{\pm}$ values of about 10^9 $L{\cdot}mol^{-1}{\cdot}s^{-1}$ (2,10) (for isobutylene) or 5 10^9 (for styrene)(2) have been measured at –80 °C in CH_2Cl_2 , CH_3Cl/hexane or $CHCl_3$/ CH_2Cl_2 solutions. These polymerizations, initiated by a halide and a Friedel Crafts activator such as $TiCl_4$ are controlled (living) in these conditions. The $k_p^{\pm}$ values were obtained by examining the competition between propagation and deactivation reactions with various nucleophiles, assuming that deactivation with the stronger nucleophiles was diffusion controlled.

The earlier methods of rate constants determination were all based on an evaluation of $[P_n^{\pm}]$, $[P_n^{+}]$ or $[P_n^{\pm}] + [P_n^{+}]$, and different initiators led to similar small values, while the very large k_ps were obtained with living systems by a completely different method. A direct comparison might be made if $[P_n^{\pm}]$ could be measured in a similar system. This is not possible with the unstable polystyryl carbocations initiated by RCl and e.g. $TiCl_4$, but kinetic data are available for indene living polymerizations.(11,12) They show that carbocations may remain stable for long times and this was confirmed recently by spectrophotometric experiments. (13) Since manageable kinetics correspond to very low concentrations of cations ($\leq 10^{-6}$ $mol{\cdot}L^{-1}$), $[P_n^{\pm}]$ was evaluated from the measured ionization equilibrium constant K_i of the monomeric model, 1-chloroindane.

Rate constants of propagation of indene on ion-pairs in CH_2Cl_2

Stable carbocations have been observed in CH_2Cl_2, after protonation of indene or its unsaturated dimer by CF_3SO_3H at –67 °C, and the molar extinction coefficient ε was equal to 16 000 $L\cdot mol^{-1}\cdot cm^{-1}$ (with the dimer and excess acid)$^{(13)}$. Ionization of 1-chloroindane by excess SbF_5 at -68 °C led to 16 000 $<\varepsilon<$20 000 for the monomeric cation $^{(14)}$. With $TiCl_4$ and $SnCl_4$, ionization was always partial, but assuming ε=16 000, K_i at –65°C could be measured since the amount of dissociated species was low at the concentration of ion-pairs present.

For the controlled polymerization of indene with CumCl and $SnCl_4$ at -40 °C (up to M_n = 1.5 10^4) the rate constants k_1 were obtained from equation (1) for a reaction first order in [M].

$$\ln [M]_o / [M]_t = k_1\, t = (k_p^{\pm} [P_n^{\pm}] + k_p^{+}[P_n^{+}])\, t \qquad (1)$$

In the presence of a salt with a common anion $SnCl_5^-$, formed with di-*tert*-butyl-methyl pyridine (DBMP) and HCl present in $SnCl_4^{(12)}$, propagation on free ions is suppressed and

$$k_1^{\pm} = k_p^{\pm} [P_n^{\pm}] \;= k_p^{\pm}\cdot K_i\,[CumCl]\,[\,SnCl_4]$$

$k_1^{\pm}$ is not available at -65 °C and it was necessary to evaluate the enthalpy of ionization ΔH_i in order to have K_i at –40 °C. When only ion-pairs are present, $k_1^{\pm}$ variation with temperature leads to a global activation energy $E_g^{\pm}$ (from the variation of ln $k_1^{\pm}$ with 1/T), which is the sum of the activation energy for propagation $E_p^{\pm}$ and of the enthalpy of ionization ΔH_i.

$$Eg^{\pm} = \Delta H_i + Ep^{\pm}$$

$Eg^{\pm}$ has been determined and is –1.4 ± 0.6 kcal $\cdot mol^{-1}$ $^{(14)}$. If $k_p^{\pm}$ is practically independent from temperature as assumed by Mayr and Faust, $Ep^{\pm}$ ~0 and Eg ~ΔH_i ~ -1 $kcal\cdot mol^{-1}$. With K_i (-65 °C) = 2 10^{-2}, this leads to K_i (-40 °C) ~1.5 10^{-2}. In the experiment at -40 °C, [CumCl] = 10^{-3} and [$SnCl_4$]= 2 10^{-3} $mol\cdot L^{-1}$, $k_1^{\pm}$ = 3.2 10^{-3} s^{-1} for the initial slope of ln M_o/M versus time (first 3 points during 1 min)$^{(12)}$.

$$[P_n^{\pm}] = K_i\,[CumCl]\,[\,SnCl_4] = 3\ 10^{-8}\ mol\cdot L^{-1} \text{ and } k_p^{\pm} = 3.2\ 10^{-3}/3\ 10^{-8} \sim 10^5\ L\cdot mol^{-1}\cdot s^{-1}.$$

It seems however quite possible that $Ep^{\pm}$ in CH_2Cl_2 might be different from zero, since Eg (derived from k_1) between 3 and 9 $kcal\cdot mol^{-1}$ have been measured for polymerizations of styrene initiated by protonic acids. According to the chosen $Ep^{\pm}$ value, in the present case

CumCl $mol \cdot L^{-1}$	MtX_n $mol \cdot L^{-1}$	$k_I^{\pm}$ s^{-1}	ΔH_i $Kcal \cdot mol^{-1}$	K_i $^{(b)}$	$[P_n^{\pm}]^{(a)}$ $mol \cdot L^{-1}$	$k_p^{\pm}$ $L \cdot mol^{-1} \cdot s^{-1}$
10^{-3}	$SnCl_4$: 2 10^{-3}	3.2 10^{-3}	0	2 10^{-2}	4 10^{-8}	8 10^{4}
			- 2.5	10^{-2}	2 10^{-8}	1.5 10^{5}
			- 5	5 10^{-3}	10^{-8}	3 10^{5}
			-10	1.5 10^{-3}	3 10^{-9}	1.1 10^{6}
5 10^{-4}	$TiCl_4$: 2 10^{-3}	2 10^{-1}	0	2 400	4.8 10^{-6}	4 10^{4}
			- 2.5	1 200	2.4 10^{-6}	8 10^{4}
			- 5	600	1.2 10^{-6}	1.6 10^{5}
			- 10	150	3 10^{-7}	7 10^{5}

Table 2: Polymerization of indene at –40°C. Propagation rate constants on ion-pairs.

a) For $SnCl_4$, $[P_n^{\pm}] = K_i$ [CumCl] $[SnCl_4]$. Reactions in presence of $HDBMP^+$, $SnCl_5^-$

For $TiCl_4$, $[P_n^{\pm}] = K_i'$ [CumCl] $[TiCl_4]^2$. Reactions in presence of Bu_4N^+, $TiCl_5^-$

b) Ki ($SnCl_4$): Equilibrium of 1st order in $[SnCl_4]$; ($TiCl_4$) : Equilibrium of 2nd order in $[TiCl_4]$

$\Delta H_i = Eg^{\pm} - Ep^{\pm}$ would vary between -1 and - 10 $kcal \cdot mol^{-1}$ when $Ep^{\pm}$ varies between 0 and 9 $kcal \cdot mol^{-1}$. This is shown Table 2 in which K_is at -40 °C were calculated from the experimental $K_i = 2\ 10^{-2}$ for 1-chloroindane at -65 °C.

However, it has been observed that reaction rates with IB of polyisobutylene chloride models $H(CH_2(CH_3)_2C)_nCl$ ionized by BCl_3 increase strongly when n increases, and this was attributed to back-strain favoring ionization(15,16). If a similar situation occurs with chloroindane and polyindene chloride dormant species, K_is used for the above calculations are too small and the $k_p^{\pm}$s would be smaller than those given in the table, which vary between 8 10^4 for $Ep^{\pm} = 1$ ($\Delta H_i = 0$) and 1.1 10^6 for $Ep^{\pm} = 9$ ($\Delta H_i = -10$).

The situation is more complex for polymerizations initiated by cumyl chloride and $TiCl_4$, since with this activator a second order in $[TiCl_4]$ has been observed for the polymerizations of isobutylene and styrene when propagation occurs on ion-pairs. This seems to indicate that propagation involves mainly active sites with $Ti_2Cl_9^-$ anions, and

$$[P_n^+, Ti_2Cl_9^-] = K_i'[CumCl]\,[TiCl_4]^2$$

For indene polymerizations at -40°C with [CumCl]=5 10^{-4} and $[TiCl_4]$=2 10^{-3} $mol \cdot L^{-1}$, in the presence of $[nBu_4N^+, TiCl_5^-]$=5 10^{-4} $mol \cdot L^{-1}$, $k_I^{\pm}$ =2 10^{-1} $s^{-1(11)}$, $[P_n^{\pm}] = K_i'[CumCl]\,[TiCl_4]^2 = 2\ 10^{-9}\ K_i'$. For 1-chloroindane, $K_i' = 2400$ at –67 °C. If the same value is assumed for the polymer end-groups and if $\Delta H_i \sim 0$, $[P^{\pm}] = 4.8\ 10^{-6}$ $mol \cdot L^{-1}$ and $k_p^{\pm} = k_I^{\pm} / [P_n^{\pm}] = 2\ 10^{-1}/4.8\ 10^{-6} \sim 4\ 10^4$ (see table 2). However, a $\Delta H_i = 0$ is still less likely than in the case of $SnCl_4$ since Eg observed with $TiCl_4$ are much more negative. For example, with indene, CumCl and $TiCl_4$ (in presence of DMSO) Eg = -4.3 kcal·mol^{-1} (11), and since Ep$^{\pm}$ should be similar with $P_n^{\pm}$ $SnCl_5^-$ (or smaller with the $Ti_2Cl_9^-$ counter ion), this may indicate that ΔH_i is of the order of -3 kcal·mol^{-1} smaller, which would lead to $k_p^{\pm}$ of the order of 10^5 (see table 2). And even if Ep$^{\pm}$ = 6 kcal·mol^{-1} (and Eg$^{\pm}$ = -4 kcal·mol^{-1}), $k_p^{\pm}$ is still lower than 10^6.

Rate constants of propagation of indene on unpaired ions

Polyindenes of high mol wts were obtained at –70 °C in CH_2Cl_2 and propagation rate constants k_I measured by calorimetry, for polymerization carried out in high purity but ''non living'' conditions (17). Initiation was probably by traces of HCl coinitiated by $TiCl_4$ (10^{-3} mol·L^{-1}; [indene] = 2 10^{-1} mol·L^{-1}), and propagation occurred predominantly on unpaired ions.

The osmotic mol wt of the polymer was 4.6 10^5 corresponding to 5 10^{-5} mol·L^{-1} of macromolecules, i.e. of dormant species P_nCl in absence of transfer.

$$[Pn^{\pm}] = K_i'[PnCl]\,[TiCl_4]^2 = 2.4\ 10^3 \times 5\ 10^{-5} \times 10^{-6} = 1.2\ 10^{-7}\ \text{mol}\cdot\text{L}^{-1}$$

For $C_7H_7^+$, $SbCl_6^-$ at -40 °C, K_D = 7 10^{-5}(18), and K_D should be similar (or larger) for $C_9H_8^+$,$Ti_2Cl_9^-$. Assuming a $K_D = 10^{-4}$ at -70 °C (ΔH_D = -1.2 kcal·mol^{-1})

$$[Pn^+] = (K_D[Pn^{\pm}])^{1/2} = (10^{-4} \times 1.2\ 10^{-7})^{1/2} = 3.5\ 10^{-6}\ \text{mol}\cdot\text{L}^{-1}$$

With k_I=1.1 s^{-1} (17), $k_p^+ = k_I/[Pn^+]$ = 3.1 10^5 L·mol^{-1}·s^{-1}. If transfer occurs, even with $k_{trM}/k_p = 10^{-4}$ (which appears to be too large (19)), only 50% of the polymer would have been formed by transfer ([P_nCl]=2.5 10^{-5} mol·L^{-1}) and k_p^+ = 6.2 10^5 L·mol^{-1}·s^{-1}. But if K_i' for the high polymer is larger than for C_9H_8Cl, k_p^+ would be reduced accordingly. The various estimated k_p^+ values are in the range calculated for $k_p^{\pm}$ with $SnCl_4$ or $TiCl_4$ at -40 °C.

Comparison of rate constants for indene and styrene

It might be considered that k_p^+ and $k_p^{\pm}$ for indene could be much lower than for styrene, this eventually resulting from steric hindrance for propagation and/or from a lower reactivity of the carbocation. But living copolymerization experiments with p-methylstyrene (pMS) (20) (more reactive than styrene) have shown that indene monomer reactivity is slightly higher than that of p-MS, which is itself twice as reactive as styrene. More significantly, rates of polymerization are independent from the relative indene / p-MS molar ratio, even for a predominant indene content (e.g up to 80%). This shows that indene homopropagation is not hampered by strong steric effects and is confirmed by the comparison of the enthalpy of polymerization ΔH_{ss} of indene (-13.9 ± 0.6 kcal·mol^{-1}, between +10 and -70 °C) with those of cyclopentadiene (-14.1 kcal·mol^{-1}) and styrene (-16 kcal·mol^{-1}) in CH_2Cl_2 with $TiCl_4$ as coinitiator. (21)

Discussion

In his last publication (22), P. H. Plesch proposes an explanation for the very large discrepancy between the k_ps obtained at -80 °C by Mayr and Faust and those measured for other "conventional polymerizations" in similar solvents. In this last case, the kinetics would involve only 1st order propagation with monomer-complexed carbocations P_n^+,M (or $P_n^{\pm}$,M), this resulting from the large monomer concentration (as for polymerization in bulk, see above). True 2nd order k_ps between active species and monomer would only be observed, as in Mayr's experiments, by extrapolation to zero [M]. But this explanation is not convincing since the k_ps of Pepper (1) and Vairon (4) were obtained for polymerizations performed at lower concentrations (0.1 to 0.25 mol·L^{-1}) than those of Mayr (10) and Faust (2) experiments (1 to 2.5 mol·L^{-1}) (2). With indene, the smaller k_ps were also obtained at low [M] ($\leq$ 0.2 mol·L^{-1}) (11,12,17). Even if there are some discrepancies between the small $k_p^{\pm}$ or k_p^+ for styrene measured in solution and derived from the evaluation of [$P_n^{\pm}$] or [P_n^+], they are of the same order of magnitude (10^4 to 10^5) as those obtained for indene living polymerization in CH_2Cl_2. This raised the question of the validity of the values, larger by a factor of 10^4 to 10^5, obtained with the same types of solvent and initiator but resulting from the competition method.

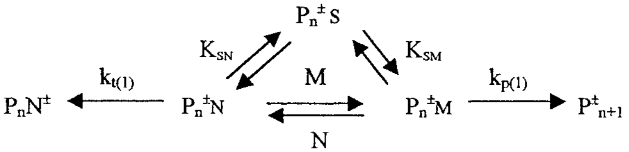
Using this indirect method for isobutylene (IB) oligomerization, diisobutylene and triisobutylene cations (DIB^+ and TIB^+) were generated by ionization of the corresponding halides by e.g. $TiCl_4$ in CH_2Cl_2 at -78 °C, and allyl silanes were used as terminators, competitively with propagation on IB (10). The TIB^+ cations react about five times faster with trimethyl (2-methylallyl)silane (a) than with IB, and assuming that the reaction of TIB^+ with this silane is diffusion controlled ($k_{deact} \sim 3\ 10^9$ L·mol^{-1}·s^{-1}) the propagation rate constant $kp^+ = 3\ 10^9/5 = 6\ 10^8$ L·mol^{-1}·s^{-1} was obtained. The ratio of the rates of addition on (a) and on trimethyl allyl silane (b) were measured for carbocations of increasing reactivity and decreased from 200 for $(4\text{-}MeC_6H_4)_2CH^+$ to 2.4 for DIB^+. The absence of selectivity of the most reactive cations was considered a proof of a diffusion-controlled reaction.

Large rate constants were also observed for deactivation of model R^+ by uncharged nucleophiles (e.g. $k^+_{deact}=10^7$ for Ph_2CH^+ and IB(24)). But these reactions involve short-lived cations (τ<80ns) eventually not yet solvated by the solvent. And k_{deact} may result from the intermediate formation of a R^+,M complex. It would not correspond to propagation, which involves monomer incorporation and formation of a new carbocation.

Faust et al measured the initial rates of the capping reaction of hydrochlorinated IB n-mers by three strong nucleophiles, 1,1-ditolyl and 1,1-dibutylethylenes, and 2-phenylfuran (2). At low concentrations of each nucleophile N, the rate was 1st order in [N] (up to $[N]\sim 5\ 10^{-3}$ mol·L^{-1}) but the order changed to near zero for $[N]\sim 10^{-1}$ mol·L^{-1}. This was attributed to a change in the rate determining step from addition to the nucleophile to ionization of the halide. Since the rates for various nucleophiles fitted on the same curve with the same limiting rate for $[N] = 10^{-1}$, this was assumed to result from diffusion-limited addition, and kp^+ was obtained from $k_{deact}= 3\cdot 10^9$ L·mol^{-1}·s^{-1}.

Another interpretation may however be proposed if propagation also occurs in two steps in solution, as suggested by Fontana(23) for propylene in solution and by Plesch (7,8) for reactions in bulk. For propagation and termination reactions, the order in M or in N would be equal to one for low concentrations of M or N (apparent first order) and become zero for sufficiently large concentrations. This was observed by Faust for $[N] \sim 0.1$ mol·L^{-1}, *nucleophile solvated species* $P_n^{\pm}N$ becoming preponderant. (15,33)

Scheme 1



As considered by Plesch with ion-pairs, one side of the carbocation plane would be occupied by the counter-ion, and the other side by a molecule of either the solvent or the monomer, these two species being in equilibrium. Propagation would only occur on *monomer solvated species* $P_n^{\pm}M$ with a 1st order rate constant $k_{p(1)}$. With the nucleophile N, a similar reaction may occur, termination giving inactive $P_nN^{\pm}$ species (see scheme 1). The polymerization rate is

$$R_p = k_p{}^{\pm}{}_{(1)}\,[P_n^{\pm}\,M] = k_p{}^{\pm}{}_{(1)}\,K_{SM}\,[P^{\pm}S]\,[M].$$

The order in monomer concentration is one but the second order rate constant $k_{p\ app} = k_p{}^{\pm}{}_{(1)}\ K_{SM}$. A similar situation may occur for termination with $R_t = k_t{}^{\pm}{}_{(1)}\,K_{SN}[P^{\pm}S]\,[N]$.

In Faust's experiments of deactivation by diarylethylenes, theoretical $M_n = [M]_{cons}/[CumCl]$ were obtained at partial conversion, showing that initiation was complete and that equilibria between dormant and active species were rapidly established. This is also the case for the equilibria between $P^{\pm}S$ and M or N. We should have $DP_n = R_p/R_t$.

$$DP_n = R_p/R_t = k_{p(1)}\, K_{SM} / k_{t(1)}\, K_{SN} \times [M]/[N]$$

In these experiments (2), $[N] = 3\ 10^{-3}$ mol·L^{-1} and it was observed that $DP_n/[M] \sim 80$. This gives, $k_{p(1)}^{\pm} K_{SM} / k_{t(1)}^{\pm} K_{SN} = 80[N] = 0.24$. It only means that the apparent rate constant $k_p{}^{\pm}{}_{app} = k_{p(1)}^{\pm} K_{SM}$ is smaller than that of termination $k_{t(1)}^{\pm} K_{SN}$, but does not give any information about the unimolecular rate constants $k_{p(1)}^{\pm}$ and $k_{t(1)}^{\pm}$ since K_{SM} and K_{SN} are also unknown. The equations - and conclusions - would be similar if competitive solvation by CH_2Cl_2 did not occur, but this hypothesis may explain more easily the large difference in rates between polymerizations in bulk and in solution.

If those preliminary solvations of $P_n^{\pm}$ or P_n^{+} by M or N occur, the unimolecular rearrangement reactions cannot be diffusion controlled and second-order $k_p^{\pm}$ or k_p^{+} values cannot be calculated using this last assumption. They can be obtained only if $[P_n^{\pm}]$ (or $[P_n^{+}]$) is known.

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