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**ADDITION REACTIONS OF CARBOCATIONS WITH ALKENES:
STUDIES ON THE MECHANISM OF CARBOCATIONIC POLYMERIZATION**

Herbert Mayr*, Reinhard Schneider, and Rudolf Pock

Institut für Chemie der Medizinischen Universität zu Lübeck
Ratzeburger Allee 160, D-2400 Lübeck 1, Federal Republic of Germany

ABSTRACT

In certain cases, Lewis acid catalyzed addition reactions of alkyl halides with alkenes terminate at the 1:1 product stage. This telomerization reaction has been employed to study the efficiency of initiating systems of carbocationic polymerization and the relative reactivities of alkenes towards carbenium ions. A direct determination of addition rate constants is possible in some cases.

INTRODUCTION

Carbocationic polymerizations, initiated by alkyl halides in the presence of Lewis acids, have acquired considerable attention in recent years since they can be employed for the formation of macromolecules with definite head and end groups [Ref.1]. Fig. 1 shows the different stages of this reaction sequence.

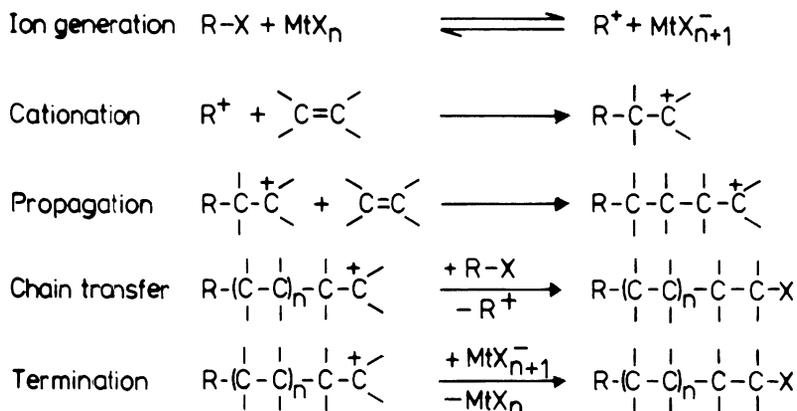
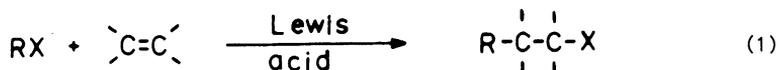


Figure 1. Mechanism of Alkyl Halide/Lewis Acid Initiated Polymerizations of Alkenes [Ref.2].

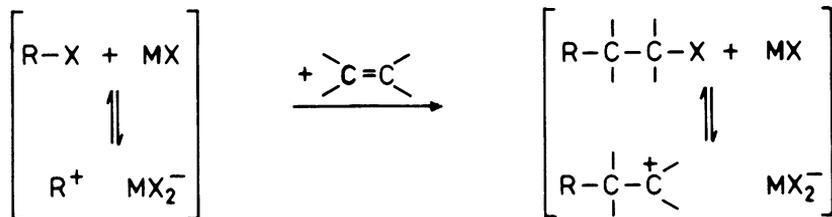
It has been reported in the literature, however, that in some cases alkyl halides and alkenes combine in the presence of Lewis acids to give [1:1] adducts (eq.1) [Ref.3]; i.e., the third part of the reaction sequence in Fig.1 has been omitted.



Since (1) appeared to be a simple model to study some aspects of carbocationic polymerization with the well established methods of physical organic chemistry, we decided to investigate the scope of reaction type 1 systematically (Chapt. 1). Its utility to solve mechanistic problems in carbocationic polymerization will be discussed in Chapters 1-3.

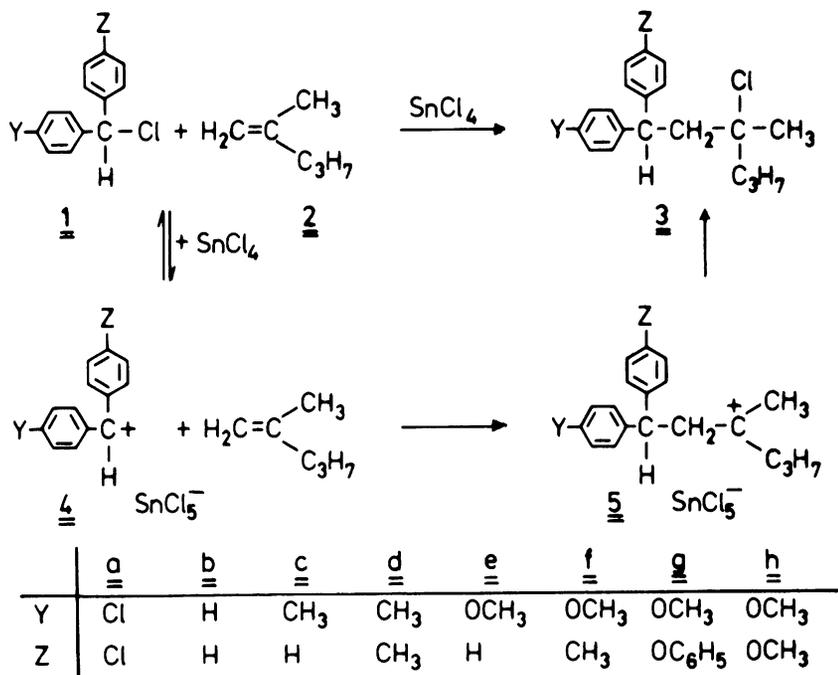
1. Development of a Reaction Model (Relative Efficiency of Initiating Systems)

If one wishes to combine alkyl halides and alkenes to give [1:1] products as shown in eq.1, the situation depicted in Scheme 1 will be encountered: Reactants as well as products are alkyl halides or carbenium ions. The selective formation of [1:1] products can, therefore, only be achieved if the system RCCX/RCC^+ is less reactive than RX/R^+ . This requirement raises the question of factors which control the reactivities of such alkyl halide/carbenium ion systems.



Scheme 1

This topic, which is also of relevance for the initiation of carbocationic polymerization, has previously been treated in different ways [Ref.4], mostly employing gas phase thermodynamic data. Their use, however, introduces an error of 10-15 kJ/mol. Since the ambiguous treatment of solvation adds to the inaccuracy of such estimates, we chose an experimental approach.



Scheme 2

The diarylmethyl chlorides 1a-h react with 2-methyl-1-pentene (2) in the presence of SnCl₄ to give the [1:1]products 3 with >90% isolated yields. Therefore, it is possible, to mix 2 with an excess of two different diarylmethyl chlorides 1y and 1z and to calculate their relative reactivity from the 3y/3z ratio.

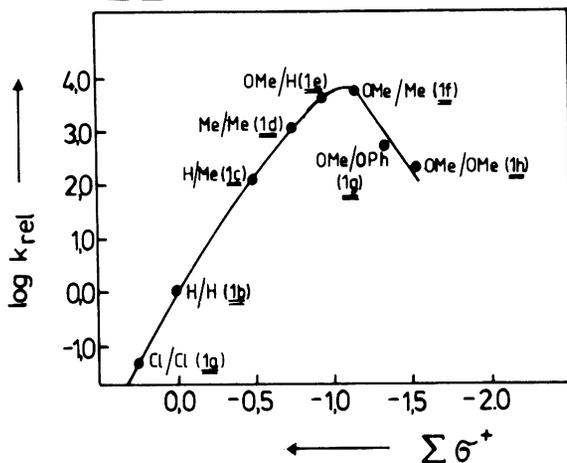


Figure 2.
Relative Reactivities of Diarylmethyl Chlorides 1a-h towards 2 in Presence of SnCl₄, ($[\text{SnCl}_4]/[\text{1}] = 2.27$)

Fig.2 shows that increasing electron donation of Y and Z enhances the reactivity by 4 orders of magnitude from 1a to 1f, where the reactivity maximum is reached. Stronger electron donation reduces the reactivity (1g,h) [Ref.5].

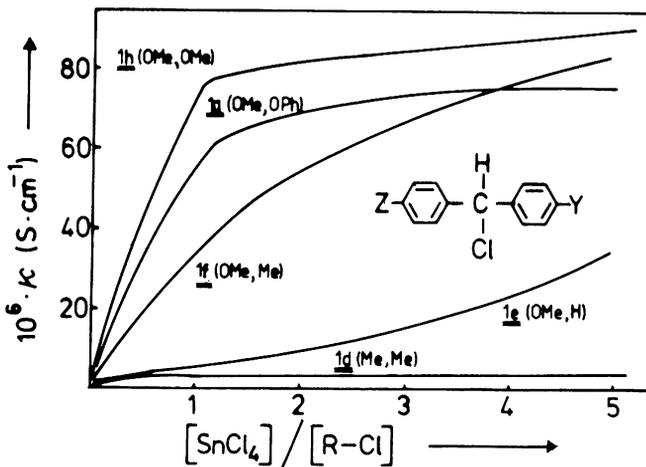


Figure 3. Conductivity Titrations of Diarylmethyl Chlorides 1d-h (~25mmol/l) with SnCl₄ in CH₂Cl₂/CH₃CO₂C₂H₅ (vol. ratio 97.5:2.5) at -78 °C.

When conductometric titrations of 1a-h with SnCl₄ were carried out under the same conditions (solvent, temperature) as the competition experiments of Fig.2, the diarylmethyl chlorides 1a-d were not significantly ionized, even when treated with 4 equivalents of SnCl₄ (Fig.3). On the other hand, 1 equivalent of SnCl₄ was sufficient to fully ionize the dimethoxy compound 1h. Fig.3 shows that 1f, the most reactive alkylating agent in this series, is considerably but not fully ionized in the presence of 1-2 equivalents of SnCl₄. This observation led to the conclusion that alkylating agents $RX \rightleftharpoons R^+$ with ΔG (ionization) = 0 possess maximal reactivity in a given Lewis acid/solvent system.

This generalization can be rationalized by inspection of the corresponding energy profiles. The situation for the Lewis acid catalyzed addition of an alkyl halide with ΔG (ionization) > 0 is depicted in Fig.4. The endergonic ionization step is followed by exergonic addition and an exergonic recombination step. Variation of Y and Z will not alter the reaction free enthalpy ΔG and, since the stabilization of the carbenium ions 5 is not influenced by the aryl substituents [Ref.6], the energy difference between 5 and 3 will be constant for all examples of Scheme 2. Consequently, the distance between 1 and 5 also has to be constant for all substitution patterns of Scheme 2.

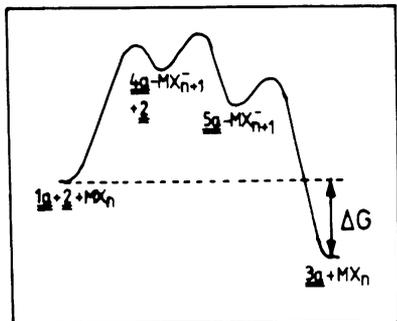


Figure 4. Energy Profile of the Lewis Acid Catalyzed Addition Reaction of an Alkyl Halide with an Alkene.

Increasing electron donation of Y and Z changes the energy profiles as shown in Fig.5 (ion combination omitted). Since only differences of ΔG are of interest, the reactants have been aligned at the same level. Since the energy difference between $\underline{1}$ and $\underline{5}$ was derived to be independent of Y and Z, all cations $\underline{5}$ will also be at the same level. As a consequence of the Bell-Evans-Polanyi principle [Ref.7], the transition states of the addition reactions will move in the same direction as $\underline{4}$, and the increase of reactivity from $\underline{1a}$ to $\underline{1f}$ is thus explained. For better electron releasing substituents, the ground state of the reactants will correspond to ionized species, and substituents influence the ground state more than the transition state. Therefore, the reaction rates decrease from $\underline{4f}$ to $\underline{4h}$.

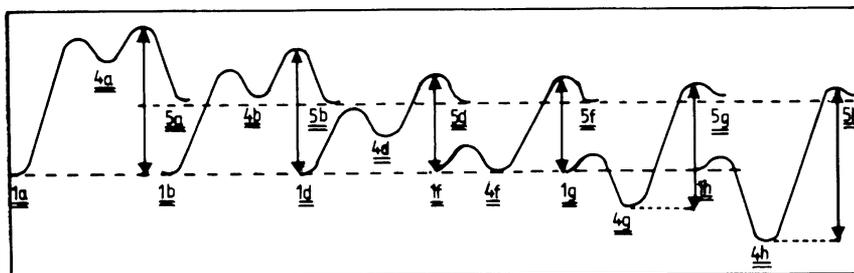


Figure 5. Schematic Energy Profiles of the Lewis Acid Catalyzed Addition Reactions of Various Alkyl Halides with a Common Alkene (For simplicity, $\underline{1} + \underline{2} + \text{MX}_n$ is replaced by $\underline{1}$, $\underline{4} - \text{MX}_{n+1}$ by $\underline{4}$, and $\underline{5} - \text{MX}_{n+1}$ by $\underline{5}$).

Our conclusion, that $\underline{1f}/\underline{4f}$ is the most reactive electrophile, was derived for a specific reaction system ($\text{SnCl}_4/\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CO}_2\text{C}_2\text{H}_5$), and it is limited to that system. If the ionizing power of the medium is increased, for example by employing a stronger Lewis acid, Fig.5 has to be replaced by Fig.6.

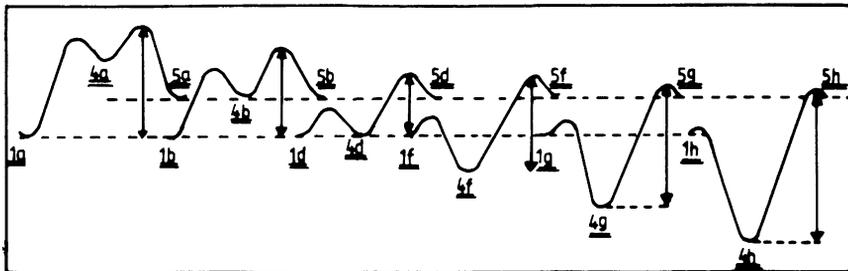


Figure 6. Schematic Energy Profiles of the Addition Reactions of Various Alkyl Halides with a Common Alkene in Presence of a Stronger Lewis Acid than that Employed for the Reactions of Fig. 5.

The reactant pair $\underline{1f/4f}$, which was approximately half ionized in Fig. 5, will almost completely be ionized in the presence of a stronger Lewis acid (Fig. 6). On the other hand, $\underline{1d/4d}$, which was ionized to a small degree by SnCl_4 (Fig. 5), may be approximately 50% ionized in the medium with stronger ionizing power (Fig. 6) and will now represent the reactivity maximum. Comparison of Figs. 5 and 6 indicates that the reactivity of fully dissociated systems like $\underline{4h}$ is not changed when the strength of the Lewis acid is varied (see Chapt. 3). On the other hand, systems with a mostly covalent ground state become more electrophilic if a stronger Lewis acid is employed. The most reactive alkylating system, which is accessible with the strong Lewis acid ($\underline{1d/4d}$, Fig. 6) corresponds to a lower ΔG^\ddagger value than the most reactive system, which is attainable with the weaker Lewis acid ($\underline{1f/4f}$, Fig. 5).

These considerations allow the systematic design of initiating systems and give a quantitative basis for the empiric rule that neither alkyl halides with very low nor alkyl halides with very high ionization tendency are efficient initiators of carbocationic polymerization [Ref. 2]. Furthermore, the introductory question of how to generate [1:1] products via eq. 1 can now be answered.

If only predominantly covalent systems are considered, one can derive from the left parts of Figs. 5 and 6 that the reactivities towards alkenes increase with decreasing ionization free enthalpies. Therefore, [1:1] products can only form selectively if $\Delta G(\text{ionization})$ of the reactants is smaller than $\Delta G(\text{ionization})$ of the products. Since ionization enthalpies have been demonstrated to be proportional to activation free enthalpies of solvolysis reactions [Ref. 8], the solvolysis data listed in Table 1 may be used to predict the outcome of reaction (1): [1:1] products can only be formed, if the functional group of the reactant is located below the functional group of the product in Table 1 [Ref. 9].

Table 1. Solvolysis Rates of some Alkyl Chlorides in 80% Aqueous Ethanol at 25°C

RX	$k_1 [s^{-1}]$
$(CH_3)_2CHCl$	$2 \cdot 10^{-9}$
$CH_2=CHCH(CH_3)Cl$	$5 \cdot 10^{-7}$
$CH_3CH=CHCH_2Cl$	$\sim 1 \cdot 10^{-6}$
$(CH_3)_3CCl$	$9 \cdot 10^{-6}$
$PhCH(CH_3)Cl$	$1 \cdot 10^{-5}$
$(CH_3)_2C=CHCH_2Cl$	$\sim 4 \cdot 10^{-4}$
$PhC=CC(CH_3)_2Cl$	$2 \cdot 10^{-3}$
$PhC(CH_3)_2Cl$	$\sim 2 \cdot 10^{-3}$
Ph_2CHCl	$2 \cdot 10^{-3}$
CH_3OCH_2Cl	15
$CH_3OCH(CH_3)Cl$	>15
$CH_3OCH(Ph)Cl$	>>15

An experimental verification of this postulate is given in Table 2, which shows the yields of [1:1]products from Lewis acid catalyzed reactions of alkyl chlorides with alkenes [Ref.10]. When alkyl halides are arranged vertically according to increasing solvolysis rates (Table 1) and alkenes are ordered horizontally in a way that solvolysis rates of the [1:1]addition products increase from left to right, a diagonal results which correlates reactants and products of equal solvolysis rates. This diagonal separates Table 2 into a lower left section where the formation of [1:1]products is observed and an upper right section where polymerization of the alkenes takes place. Similar results were found for allyl [Ref.11] and propargyl halide [Ref.12] additions. The more complex situations, which arise if reactants and products with $\Delta G(\text{ionization}) < 0$ are not excluded, will be discussed in a subsequent paper.

Table 2. Yields of [1:1]Products of Lewis Acid Catalyzed Addition Reactions of Alkyl Halides with Alkenes (Predictions in Parentheses) [Ref.10]

RCI	$H_2C=\overset{CH_3}{C}$	$H_2C=\overset{HC=CH_2}{C}$	$H_2C=C(CH_3)_2$	$H_2C=CHPh$	$H_2C=\overset{HC=CH_2}{C}-CH_3$	$H_2C=\overset{Ph}{C}-CH_3$	$H_2C=\overset{OC_2H_5}{C}-CH_3$
$(CH_3)_2CHCl$	—	—	—	(—)	—	—	(—)
$(CH_3)_3CCl$	41	35	—	—	—	(—)	(—)
$PhCH(CH_3)Cl$	52	50	71	72	—	—	(—)
$PhC\equiv C(CH_3)_2Cl$	67	46	93	91	67	—	—
$PhC(CH_3)_2Cl$	58	65	71	71	64	58	—
Ph_2CHCl	92	85	97	88	82	75	—
CH_3OCH_2Cl	47	70	60	75	64	37	—
$CH_3OCH(Ph)Cl$	78	65	90	57	52	69	68

2. Relative Alkene Reactivities (Carbocationic Copolymerization)

A simplified treatment of propagation in carbocationic copolymerization, which only considers the last monomer unit of the growing cation, is shown in Fig.7. The determination of the reactivity ratios r_A and r_B by the conventional methods is tedious [Ref.13a], and attempts have been made to predict relative alkene reactivities theoretically [Ref.13b].

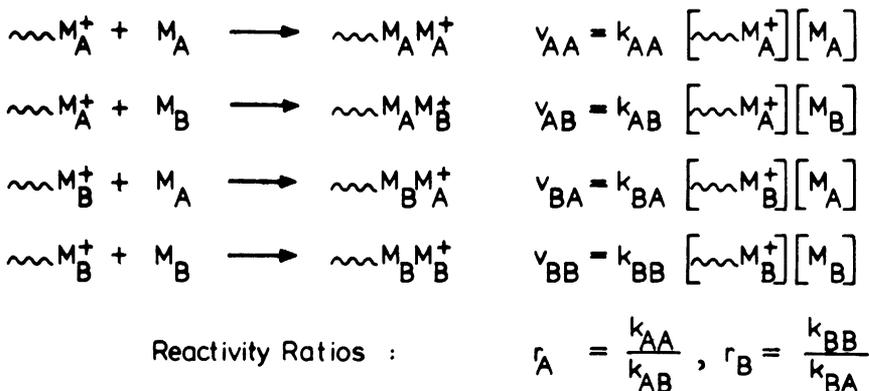
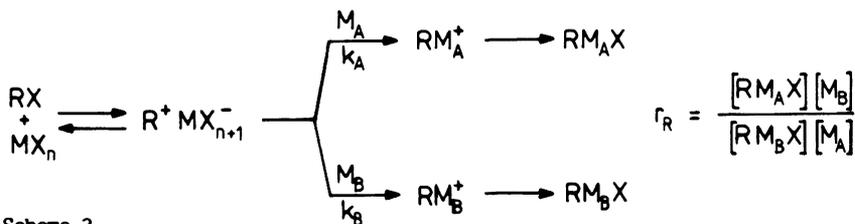


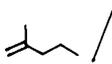
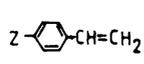
Figure 7. Propagation Steps in Carbocationic Copolymerization of Two Monomers.

Since it was shown above that alkyl halides can be reacted with alkenes to give [1:1]products, a new method for the determination of r values is now available. One can generate carbenium ions R^+ in the presence of two alkenes M_A and M_B , as shown in Scheme 3, and derive their relative reactivities from the yields of the [1:1]products. If a large excess of M_A and M_B over RX is used, so that the M_A/M_B ratio remains almost constant during the reaction, the relative reactivity of M_A and M_B towards R^+ can be calculated by the simple formula in Scheme 3. If the excess of alkenes over RX is not sufficiently high, the change of the M_A/M_B ratio during the reaction has to be taken into account as described previously [Ref.14]. R^+ , counter ions, and solvents can be varied within a wide range, and the influence of these parameters on the reactivity ratio of the monomers can be determined conveniently.



When mixtures of 2-methyl-1-pentene (2) and of one of the styrenes in Table 3 were treated with di(p-tolyl)methyl chloride (1d) in the presence of $ZnCl_2/Et_2O$, the reactivity ratios listed in Table 3 were obtained. As expected from the negative σ^+ value of fluorine, p-fluorostyrene reacts faster with 4d than the unsubstituted styrene. In contrast, p-fluorostyrene was reported to be less reactive towards trityl hexachloroantimonate than styrene [Ref.15]. p-Chlorostyrene and p-bromostyrene turned out to be equally reactive, as previously found in carbocationic copolymerization of these two monomers ($r_1=r_2=1.0$) [Ref.13a].

Table 3. Relative Reactivities towards Di(p-tolyl)methyl Chloride/ $ZnCl_2$ - Et_2O in CH_2Cl_2 at $-70^\circ C$

Z	F	H	Cl	Br
k  / k 	3.6	4.0	15.0	15.0

r_1 -Values from 1.7 to 2.7 and $1/r_2$ values from 1.8 to 3.3, which were reported for the copolymerization of styrene and p-chlorostyrene in CCl_4 /nitrobenzene mixtures at $0^\circ C$ [Ref.16], should be compared with the reactivity ratio of 3.7 (= 15:4) from Table 3.

An r_1 value of 4.48 was determined for the $TiCl_4$ initiated copolymerization of isobutene and styrene in dichloromethane at $-20^\circ C$ [Ref.13a], which is closely similar to the reactivity ratio of 2-methyl-1-pentene (2) and styrene reported in Table 3. However, the r values of the isobutene/styrene copolymerization appear to be strongly dependent on the reaction conditions, and it should be examined if the reactivity ratios of Table 3 are subject to similar effects.

The data in Table 4, which compares the relative reactivities of 2-methyl-1-pentene (2) and isoprene with respect to several electrophiles, indicates that the relative stabilities of the cations formed in the addition reactions, cannot be the only factor determining alkene reactivities. Though 1,1-dialkylated allyl cations are better stabilized than tertiary alkyl cations [17], isoprene is approximately 1.6 times less reactive than 2. A reactivity ratio of 1.3 was reported for isobutene/isoprene with respect to 4b in dichloroethane at $24^\circ C$ [Ref.18]. In accordance with these findings, isobutene has been reported to be slightly more reactive than isoprene in cationic copolymerization ($r_1=2.5$, $1/r_2=2.5$, $AlCl_3$, CH_2Cl_2 , $-103^\circ C$). [Ref.13a].

Table 4. Relative Reactivities of 2-Methyl-1-pentene and Isoprene towards Diarylmethyl Cations in Dichloromethane at -70°C

$\text{Ar}_2\text{CH}^+ \text{X}^-$	<u>1b</u> - ZnCl_3^-	<u>1d</u> - ZnCl_3^-	<u>1e</u> - BCl_4^-
	1.65 - 2.00	1.67	1.60

Relative alkene reactivities have provided information about transition state structures of electrophilic addition reactions. The similar bromination rates of the two butene isomers in Fig.8 are in accordance with a bridged transition state, since the methyl groups exert nearly the same stabilizing effects in either position. In contrast, isobutene undergoes proton catalyzed hydration much faster than propene and *cis*-butene, indicating an acyclic transition state, where only the methyl groups at the carbenium center are of importance.

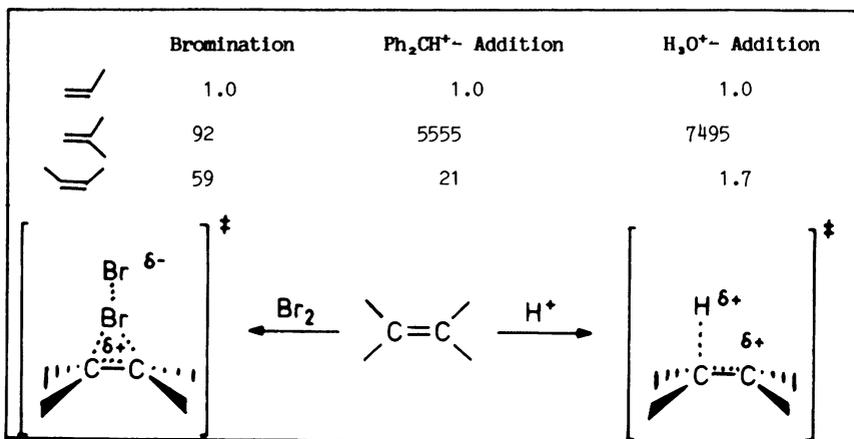
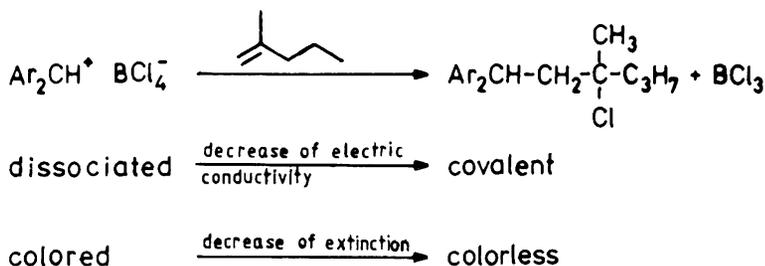


Figure 8. Relative Reactivities and Transition State Structures in Electrophilic Bromination [Ref.19], Proton Catalyzed Hydration [Ref.20], and Benzhydryl Cation Addition [Ref.14].

Like proton additions, the benzhydryl cation additions are strongly accelerated by methyl groups at the developing carbenium center (Fig.8). The reactivity increase from propene to *cis*-butene may be due to the reduction of the HOMO(alkene)-LUMO(Ph_2CH^+) energy difference (frontier orbital term [Ref.21]). Alternatively, the reactivity difference of *cis*-butene and propene could be explained by a partially bridged transition state, in which the attacked position of the alkene carries part of the positive charge.

3. Determination of Absolute Addition Rates

In addition to the investigation of relative RX/R^+ reactivities (Chapt. 1) and alkene reactivities (Chapt. 2) by competition experiments, a modification of the model reaction (1) allows the direct determination of addition rates of certain carbenium ions to alkenes. The diarylcarbenium tetrachloroborates $\underline{4d-h} - BCl_4^-$, which can be prepared in dichloromethane solution, combine with $\underline{2}$ to give covalent [1:1]products (Scheme 4). The rates of these reactions can be monitored conductometrically and photometrically.



Scheme 4

The reactions were found to be of first order with respect to $\underline{4} - BCl_4^-$ and of first order with respect to olefin, like the initiation of p-methoxystyrene polymerization with trityl hexachloroantimonate [Ref.22]. Since $\underline{4h} - BCl_4^-$ ($k_2 = 2.9 \cdot 10^{-2} \text{ l mol}^{-1} \text{ s}^{-1}$), $\underline{4h} - BBr_3Cl^-$ ($2.7 \cdot 10^{-2}$), and $\underline{4h} - SnCl_5^-$ ($2.5 \cdot 10^{-2}$) show similar reactivities towards $\underline{2}$, we may assume that specific ion pairs do not exist under these conditions. Alternatively we must conclude that free ions and various types of ion pairs do not differ in their reactivity.

Table 5. Rate Constants ($\text{CH}_2\text{Cl}_2, -70^\circ\text{C}$) and Activation Parameters of the Reactions of Diarylcarbenium Tetrachloroborates with 2-Methyl-1-pentene($\underline{2}$). [Ref.23]

	Y	Z	k_2 (l/mol s)	ΔH^* (kJ/mol)	ΔS^* (J/mol K)	$\Delta G^*(-70^\circ\text{C})$ (kJ/mol)
$\underline{4h}$	OCH_3	OCH_3	$2.9 \cdot 10^{-2}$	29.8	-125	55.1
$\underline{4g}$	OCH_3	OPh	$1.7 \cdot 10^{-1}$			51.9
$\underline{4f}$	OCH_3	CH_3	3.4	22.7	-120	47.1
$\underline{4e}$	OCH_3	H	$2.4 \cdot 10^1$	18.8	-122	43.6
$\underline{4d}$	CH_3	CH_3	$3.6 \cdot 10^3$	11.6	-117	35.4

As expected from the right parts of Figs. 5 and 6, the reactivities of $\underline{4}$ increase with decreasing electron donation of Y and Z (Table 5). The reactions of the less stabilized carbenium ions ($\underline{4d,e}$) are predominantly entropy

controlled. Variation of Y and Z exerts its major influence on ΔH^* , whereas ΔS^* is not significantly affected.

Replacement of the methyl group in 4f by hydrogen (\rightarrow 4e) lowers ΔH^* by 5.2 kJ/mol. If similar methyl effects are assumed for the comparison 4d \rightarrow 4b (probably it will be greater because of the stronger electron deficiency), a ΔH^* value < 0 is estimated for the reaction of 4b with 2. Since tertiary alkyl cations are more reactive than the diphenylmethyl cation (4b), we expect a zero or negative activation enthalpy for the cationic polymerization (propagation) of 2 under these conditions.

4. Outlook

Models can never entirely take the place of the real object. Without any doubt, there is some difference in behaviour between a polymeric cation and its low molecular weight model, e.g., the propagating species in isobutene polymerization and the tert.-butyl cation. The question is: How big is this difference? How close can we get to reality?

The same carbenium ions 4, which have been used in the model reactions, can be employed as initiators of carbocationic polymerizations. One only has to suppress the immediate termination by either increasing the alkene concentration or by making use of less nucleophilic counter ions. Since the reaction rates of Table 8 were not influenced by the nature of the counter ions used so far, we are confident that such data represents good approximations for initiation rates.

A fundamental problem prevents the construction of appropriate models for the propagation steps of carbocationic polymerization: Since reactants and products are structurally identical, one cannot terminate the reactions at the [1:1]product stage selectively (Chapt.1). Information about the propagation of an alkene $H_2C=CHX$ could be obtained, however, by reacting $H_2C=CHX$ with a series of carbenium ions R_1^+ , R_2^+ R_n^+ and by extrapolating to the reactivity of $H_3C-\overset{+}{C}HX$ by means of linear free energy relationships. A similar procedure may be used to modify the relative reactivities of Chapter 2 into reactivity ratios relevant for copolymerization.

Models are of minor complexity than the reality they stand for. Therefore, these studies, which deliver clear information very rapidly, may help to deepen our understanding for structural and medium effects in carbocationic polymerization and thus even the way for the production of tailor made polymers.

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