

The efficiency of alkyl halide initiators in carbocationic polymerization

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Introduction

Combinations of alkyl halides and Lewis acids¹⁾ gain increasing importance as initiating systems of carbocationic polymerization since they allow the production of macromolecules with discretionary molecular weight and definite head groups²⁾. Initiation by these systems has been considered to take place in two steps, ion generation (Eq. (1)) and cationation (Eq. (2))^{2,3)}.



This scheme has been used to explain qualitatively that neither alkyl halides yielding very unstable (i. e. reactive) carbenium ions nor alkyl halides yielding very stable (i. e. unreactive) carbenium ions are efficient initiators. In the first case step (1) and in the second case step (2) is unfavorable^{2,3)}. Other authors criticized this conclusion and offered alternative interpretations for the experimental data⁴⁾. We now present a theoretical analysis of the initiation efficiency of such systems⁵⁾ and corroborate our conclusions by direct determination of relative initiation rates of alkyl halide/Lewis acid combinations.

Results and discussion

Fig. 1 shows schematic energy profiles for the additions of various alkyl halides $R-X$ to a certain alkene. As discussed earlier⁶⁾, the energy of $R-\overset{\overset{|}{\text{C}}}{\underset{\underset{|}{\text{C}}}{\text{C}}}^+ MtX_{n+1}^-$ relative to the reagents (ΔG in Fig. 1) depends on the substituents of the alkene and the ionizing power of the medium (Lewis acid, solvent), but is almost independent of R . With ΔG being constant, it is derived from the Bell-Evans-Polanyi principle⁷⁾, that the height of the addition transition state decreases with increasing stability of R^+ ($R_A \rightarrow R_E$). If the ground state of the reagents corresponds to predominantly undissociated material ($RX + MtX_n$), a stabilization of R^+ causes a decrease of ΔG^* ($\Delta G_A^* \rightarrow \Delta G_C^*$). Further stabilization of R^+ ($R_C^+ \rightarrow R_E^+$) lowers the ground state of the reactants ($R^+ MtX_{n+1}^-$) more than the transition state, resulting in an increase of

the activation energy. The minimum of ΔG^\ddagger corresponds to a reactant system with ΔG (dissociation) = 0 (R_C^\ddagger/R_CX in Fig. 1).

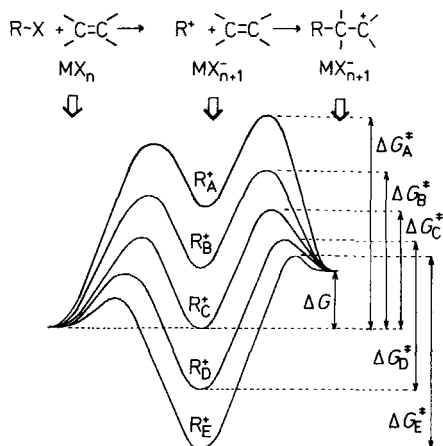
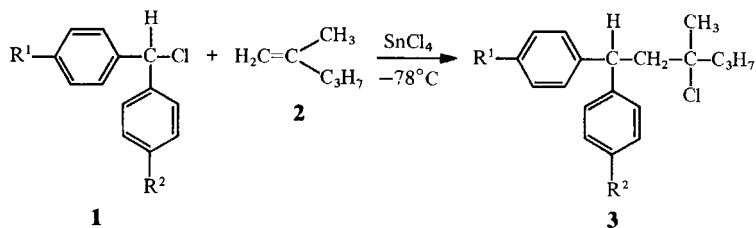


Fig. 1. Schematic energy profiles for the Lewis acid initiated additions of various alkyl halides to a constant alkene

For an experimental test of this model we studied the relative reactivities of a series of diarylmethyl chlorides **1a–h** toward 2-methyl-1-pentene (**2**) ($SnCl_4$ -catalysis; $-78^\circ C$). We selected reaction conditions under which the telomerisations stop after inclusion of a single alkene unit⁶.



	1a, 3a	b	c	d	e	f	g	h
R^1	Cl	H	CH ₃	CH ₃	OCH ₃	OCH ₃	OCH ₃	OCH ₃
R^2	Cl	H	H	CH ₃	H	CH ₃	OC ₆ H ₅	OCH ₃

On a preparative scale, **3a–h** were isolated in a yield $>90\%$. Therefore, it is possible to obtain the relative reactivities of **1a–h** from competition experiments by determining the 1:1 adduct (**3a–h**) ratios. Since the variation of the substituents is far remote from the reacting centers, the constancy of ΔG (Fig. 1) is readily fulfilled in all these systems.

Fig. 2 shows that increasing electron donation of R^1 and R^2 enhances the reactivity from **1a** to **1f** by 4 orders of magnitude. Stronger electron donation reduces the

reaction rates (**1g**, **h**). Compound **1f** with anisyl and tolyl residues, the most reactive system, should correspond to R_CX in Fig. 1 and should, therefore, be approximately half dissociated under the reaction conditions.

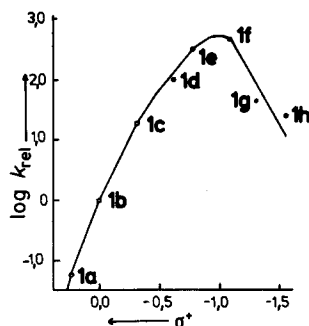


Fig. 2. Relative reactivities of diarylmethyl chlorides **1a** – **h** toward 2-methyl-1-pentene (SnCl_4 -catalysis)

This hypothesis could be verified by means of conductometric titrations of **1a** – **h** with SnCl_4 . Fig. 3 shows that compounds **1a** – **d** are not noticeably dissociated in the presence of 1 equivalent of SnCl_4 . On the other hand, 1 equivalent of Lewis acid is sufficient to fully ionize the dianisyl compound **1h**. Though a quantitative evaluation of Fig. 3 is not possible without determining the degree of ion pairing, it is obvious that **1f** is considerably but not fully dissociated in the range of the competition experiments.

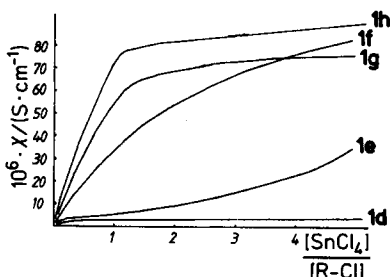


Fig. 3. Conductivity titrations of diarylmethyl chlorides **1d** – **h** (~25 mmol/l) with SnCl_4 in $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CO}_2\text{CH}_3$ (vol. ratio 97,5:2,5) at -78°C

Experimental part

2-Methyl-1-pentene (**2**) (from EGA-Chemie; 99% GC) was used without further purification. Compounds **1a** – **h** were prepared by treatment of the corresponding diarylmethanols with gaseous HCl in petroleum ether according to literature procedures⁸⁾ (purification by distillation or recrystallization from petroleum ether). CH_2Cl_2 was washed with conc. H_2SO_4 , 5% Na_2CO_3 -solution, and water, dried over CaCl_2 and distilled over P_2O_5 . Ethyl acetate was dried over CaCl_2 and distilled over P_2O_5 . SnCl_4 was refluxed over Sn -pellets and distilled in a nitrogen atmosphere.

Typical procedure for the preparation of 3a – h: 2,17 g (10,0 mmol) of **1c** and 0,30 ml (2,6 mmol) of SnCl_4 were dissolved in 50 ml of CH_2Cl_2 and 1,5 ml of ethyl acetate at -78°C . A solution of 1,00 g (11,0 mmol) of **2** in 10 ml of CH_2Cl_2 was added dropwise within 10 min. After 4 h at -78°C , SnCl_4 was extracted with 2 N HCl , the organic layer dried over CaCl_2 and the

solvent evaporated at ambient temperature. The remaining oil (2,90 g, 96%) was identified to be pure **3c** by ^1H NMR and HPLC.

The competition experiments were carried out at -78°C in 97,5% CH_2Cl_2 /2,5% $\text{CH}_3\text{CO}_2\text{Et}$ (if pure CH_2Cl_2 is used as solvent, precipitation occurs in some cases). Mixtures of two diarylchloromethanes **1** were dissolved in CH_2Cl_2 / $\text{CH}_3\text{CO}_2\text{Et}$ (15–120 mmol/l), cooled to -78°C , and SnCl_4 (45,5 mmol/l) was added. 2-Methyl-1-pentene (3,9–7,8 mmol/l) was added to the clear solution. After completion of the reaction, the Lewis acid was washed out with conc. aqueous ammonia. Product analysis (HPLC) and evaluation were carried out as described previously⁹⁾.

As expected, the relative reactivities of the readily ionizing compounds **1e–h** depend on the $[\text{SnCl}_4]/[\mathbf{1}]$ ratio. The corresponding data in Fig. 2 refer to $[\mathbf{1e–h}] = 20$ mmol/l, i.e. $[\text{SnCl}_4]/[\mathbf{1}] = 2,27$.

The conductivity titrations were carried out with a Wayne Kerr Autobalance Universal Bridge B 642.

Conclusion

For a given ionizing power of the medium (Lewis acid, solvent) a half dissociated alkyl halide/carbenium ion system is the most active initiator. Its activity cannot be considerably enhanced by using a stronger Lewis acid since both $\text{R}^+\text{MtX}_{n+1}^-$ and $\text{R}-\overset{+}{\text{C}}\text{C} \lt \text{MtX}_{n+1}^-$ will be stabilized to a similar amount so that ΔG^\ddagger remains almost constant (Fig. 1). In the case of predominantly unionized reactants ($\text{R}_\text{A}\text{X}$, $\text{R}_\text{B}\text{X}$ in Fig. 1), stronger Lewis acids will, however, increase the reactivity of the system, since now the energy content of the ionic intermediates decreases while the ground state of the reactants remains unchanged. Therefore, if a 50% dissociated alkyl halide/Lewis acid pair does not efficiently initiate polymerization of a certain alkene, one may apply a stronger Lewis acid and simultaneously switch to a less readily ionizing alkyl halide.

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- 1) According to Kennedy's nomenclature (ref. 2, p. 11), alkyl halides are termed "initiators" and Lewis acids "coinitiators"
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