

## The efficiency of alkyl halide initiators in carbocationic polymerization

Herbert Mayr\*, Reinhard Schneider

Institut für Organische Chemie der Friedrich-Alexander-Universität Erlangen-Nürnberg,  
D-8520 Erlangen, Federal Republic of Germany

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### Introduction

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



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<sup>2,3)</sup>. Other authors criticized this conclusion and offered alternative interpretations for the experimental data<sup>4)</sup>. We now present a theoretical analysis of the initiation efficiency of such systems<sup>5)</sup> 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 earlier<sup>6)</sup>, the energy of  $R-\overset{\overset{|}{\text{C}}}{\underset{\underset{|}{\text{C}}}{\text{C}}}^+ MtX_{n+1}^-$  relative to the reagents ( $\Delta G$  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  $\Delta G$  being constant, it is derived from the Bell-Evans-Polanyi principle<sup>7)</sup>, 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  $\Delta G^*$  ( $\Delta G_A^* \rightarrow \Delta G_C^*$ ). 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  $\Delta G^\ddagger$  corresponds to a reactant system with  $\Delta G$  (dissociation) = 0 ( $R_C^\ddagger/R_CX$  in Fig. 1).

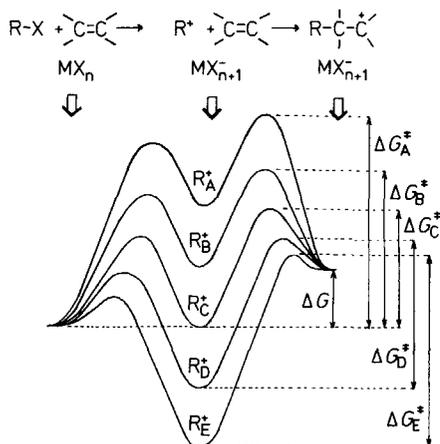
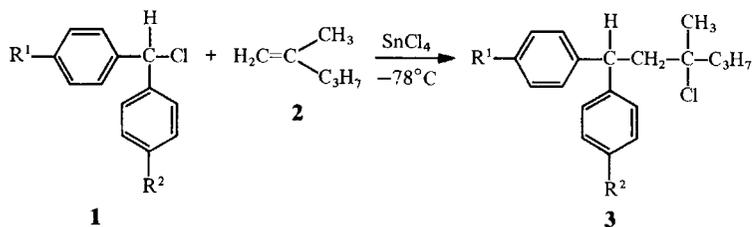


Fig. 1. Schematic energy profiles for the Lewis acid initiated additions of various alkyl halides to a constant alkene

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**) ( $\text{SnCl}_4$ -catalysis;  $-78^\circ\text{C}$ ). We selected reaction conditions under which the telomerisations stop after inclusion of a single alkene unit<sup>6</sup>.



|              | <b>1a, 3a</b> | <b>b</b> | <b>c</b>      | <b>d</b>      | <b>e</b>       | <b>f</b>       | <b>g</b>                | <b>h</b>       |
|--------------|---------------|----------|---------------|---------------|----------------|----------------|-------------------------|----------------|
| $\text{R}^1$ | Cl            | H        | $\text{CH}_3$ | $\text{CH}_3$ | $\text{OCH}_3$ | $\text{OCH}_3$ | $\text{OCH}_3$          | $\text{OCH}_3$ |
| $\text{R}^2$ | Cl            | H        | H             | $\text{CH}_3$ | H              | $\text{CH}_3$  | $\text{OC}_6\text{H}_5$ | $\text{OCH}_3$ |

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  $\Delta G$  (Fig. 1) is readily fulfilled in all these systems.

Fig. 2 shows that increasing electron donation of  $\text{R}^1$  and  $\text{R}^2$  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.

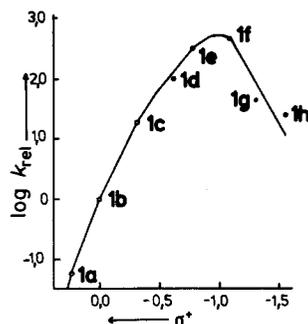


Fig. 2. Relative reactivities of diarylmethyl chlorides **1a** – **h** toward 2-methyl-1-pentene ( $\text{SnCl}_4$ -catalysis)

This hypothesis could be verified by means of conductometric titrations of **1a** – **h** with  $\text{SnCl}_4$ . Fig. 3 shows that compounds **1a** – **d** are not noticeably dissociated in the presence of 1 equivalent of  $\text{SnCl}_4$ . 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.

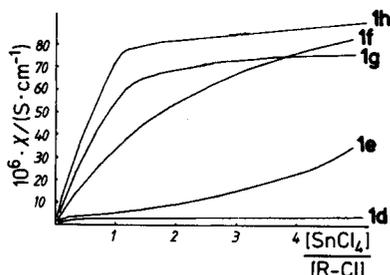


Fig. 3. Conductivity titrations of diarylmethyl chlorides **1d** – **h** (~25 mmol/l) with  $\text{SnCl}_4$  in  $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CO}_2\text{CH}_3$  (vol. ratio 97,5:2,5) at  $-78^\circ\text{C}$

## 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 procedures<sup>8)</sup> (purification by distillation or recrystallization from petroleum ether).  $\text{CH}_2\text{Cl}_2$  was washed with conc.  $\text{H}_2\text{SO}_4$ , 5%  $\text{Na}_2\text{CO}_3$ -solution, and water, dried over  $\text{CaCl}_2$  and distilled over  $\text{P}_2\text{O}_5$ . Ethyl acetate was dried over  $\text{CaCl}_2$  and distilled over  $\text{P}_2\text{O}_5$ .  $\text{SnCl}_4$  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  $\text{SnCl}_4$  were dissolved in 50 ml of  $\text{CH}_2\text{Cl}_2$  and 1,5 ml of ethyl acetate at  $-78^\circ\text{C}$ . A solution of 1,00 g (11,0 mmol) of **2** in 10 ml of  $\text{CH}_2\text{Cl}_2$  was added dropwise within 10 min. After 4 h at  $-78^\circ\text{C}$ ,  $\text{SnCl}_4$  was extracted with 2 N HCl, the organic layer dried over  $\text{CaCl}_2$  and the

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

The competition experiments were carried out at  $-78^\circ\text{C}$  in 97,5%  $\text{CH}_2\text{Cl}_2$ /2,5%  $\text{CH}_3\text{CO}_2\text{Et}$  (if pure  $\text{CH}_2\text{Cl}_2$  is used as solvent, precipitation occurs in some cases). Mixtures of two diarylchloromethanes **1** were dissolved in  $\text{CH}_2\text{Cl}_2$ / $\text{CH}_3\text{CO}_2\text{Et}$  (15–120 mmol/l), cooled to  $-78^\circ\text{C}$ , and  $\text{SnCl}_4$  (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 previously<sup>9)</sup>.

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  $\Delta G^\ddagger$  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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- 9) H. Mayr, R. Pock, *Tetrahedron Lett.* **1983**, 2155