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A Novel Method for the Determination of Propagation Rate Constants: Carbocationic Oligomerization of Isobutylene[†]

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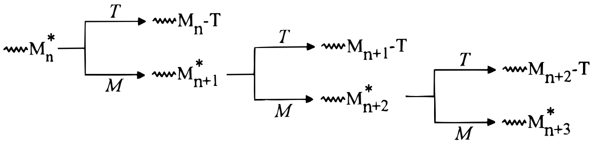
ABSTRACT: The tertiary carbenium ions $\mathbf{2}^+$ and $\mathbf{3}^+$, models of the propagating species in carbocationic isobutylene polymerization, are generated from the tertiary chlorides **2c** and **3c** with a Lewis acid in the presence of isobutylene (**1c**) and one of the allylsilanes **1a** or **1b**, which act as terminators. Since the rate of the termination reaction is known, the ratio of the telomerization products can be evaluated to give a propagation rate constant of $(6 \pm 2) \times 10^8$ L mol^{-1} s^{-1} (independent of temperature) for the carbocationic oligomerization of isobutylene in dichloromethane.

Introduction

The knowledge of the rate constants of the individual steps of a polymerization reaction is the key to an efficient control of such processes.[1] Numerous attempts to determine the propagation rate constants of the cationic polymerization of isobutylene yielded values from 6×10^3 to 1.5×10^8 L mol^{-1} s^{-1}.[2−8] While Marek reported a value of 6×10^3 L mol^{-1} s^{-1} for the $AlCl_3$/$TiCl_4$-initiated polymerization in heptane[2] and a value of 7.9×10^5 L mol^{-1} s^{-1} for the light-induced bulk polymerization with VCl_4,[3] Giusti determined a rate constant of 1.2×10^4 L mol^{-1} s^{-1} for the polymerization in methyl chloride with Et_2AlCl/Cl_2 as initiating system.[4] Plesch calculated a propagation rate constant of 9.1×10^3 L mol^{-1} s^{-1} from Ueno's polymerizations of isobutylene in methylene chloride with ionizing radiation as a source for carbocations,[1,5] whereas the bulk polymerization of Taylor yielded a value of 1.5×10^8 L mol^{-1} s^{-1}.[6] The problem of determining reliable k_p^+ values was emphasized by Plesch,[1] who carefully examined the published propagation rate constants of the cationic polymerization of alkenes and in the end accepted only 15 values for 5 monomers as well founded and credible. Since previous investigations in this laboratory have shown that the rates of attack of carbocations at alkenes depend little on solvent polarity and are independent of the nature of counter ions,[9,10] we have decided to tackle this problem with different methods.

We now present a novel and general approach for the determination of propagation rate constants in homopolymerizations. It is based on the selectivity of the propagating chain end (~~M*) for the monomer (M) and a trapping agent (T) which is known to react with diffusion control (Scheme 1).

Scheme 1



In previous work, we have shown that the reactions of carbocations with nucleophiles follow linear free energy relationships if $k < 5 \times 10^7$ L mol^{-1} s^{-1}, while deviations from the linear correlations are observed when faster reactions are considered.[11] As a consequence, the stabilized carbocations on the left side of Figure 1 follow so-called constant selectivity relationships and all of them react 10^3 times faster with 2-methallyltrimethylsilane (**1a**) than with allyltrimethylsilane (**1b**). As one moves to the right side of Figure 1 and considers less stabilized and more reactive carbocations, the selectivity decreases and finally disappears when both competing reactions become diffusion controlled. We have discussed that the relative reactivity of **1a** and **1b** toward $\mathbf{2}^+$ ($k_a/k_b = 2.4$) indicates diffusion control of the reaction of $\mathbf{2}^+$ with **1a**, the faster of the two competitors.[12] The rate constant for the slower reaction (k_b) can then be calculated from the known value for diffusion control ($k_a \approx 3 \times 10^9$ L mol^{-1} s^{-1}) and the competition constant k_a/k_b.

We now employ this so-called diffusion clock method[13−16] to determine the propagation rate constant for the carbocationic oligomerization of isobutylene.

Results

Diisobutylene hydrochloride (**2c**), which was obtained by hydrogen chloride addition to the commercially available diisobutylene (**2a**), reacts with the allylsilanes **1a** and **1b** in the presence of $TiCl_4$ to give 91 and 86% of the terminal olefins **3a** and **3b**,[17−19] respectively. Addition of hydrogen chloride to **3a** yields the tertiary chloride **3c**, which is analogously converted into the compounds **4a** and **4b**. Another repetition of this sequence gives rise to the higher homologues **5a** and **5b** (Scheme 2).

The high yields of the allylation reactions reported in Scheme 2 have been obtained in dichloromethane solution by combining the tertiary chlorides **2c**, **3c**, or **4c** with 0.25−2 equiv of $TiCl_4$ and 3−6 equiv of the allylsilanes **1a** or **1b**. The reaction of **2c** with **1b** has also been achieved with $AlCl_3$ in dichloromethane or with $TiCl_4$ in *n*-hexane. Attempts to produce **3b** by BCl_3- or $ZnCl_2 \cdot OEt_2$-promoted reactions of **2c** with **1b** in dichloromethane were not successful, however. While the decomposition of **1b** by BCl_3 is faster than the BCl_3-catalyzed reaction of **2c** with **1b**, no reaction took place in the presence of the weak Lewis acid $ZnCl_2 \cdot OEt_2$.

Competition experiments as illustrated in Scheme 3 were performed to determine the relative reactivities (k_a/k_b) of the allylsilanes **1a** and **1b** toward the carboca-

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[†] This and the succeeding paper are dedicated to Professor R. Gompper on the occasion of his 70th birthday.

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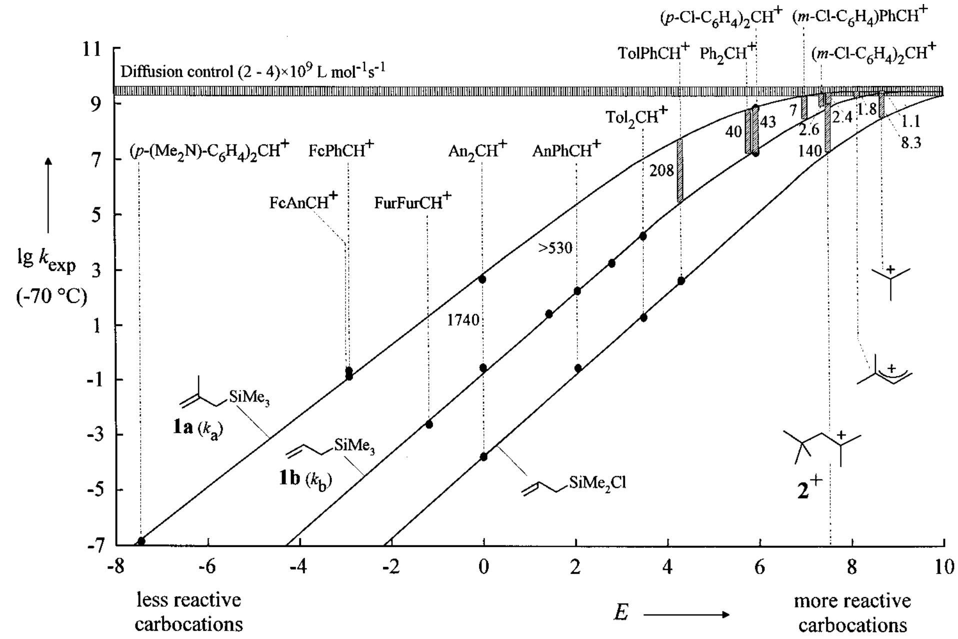
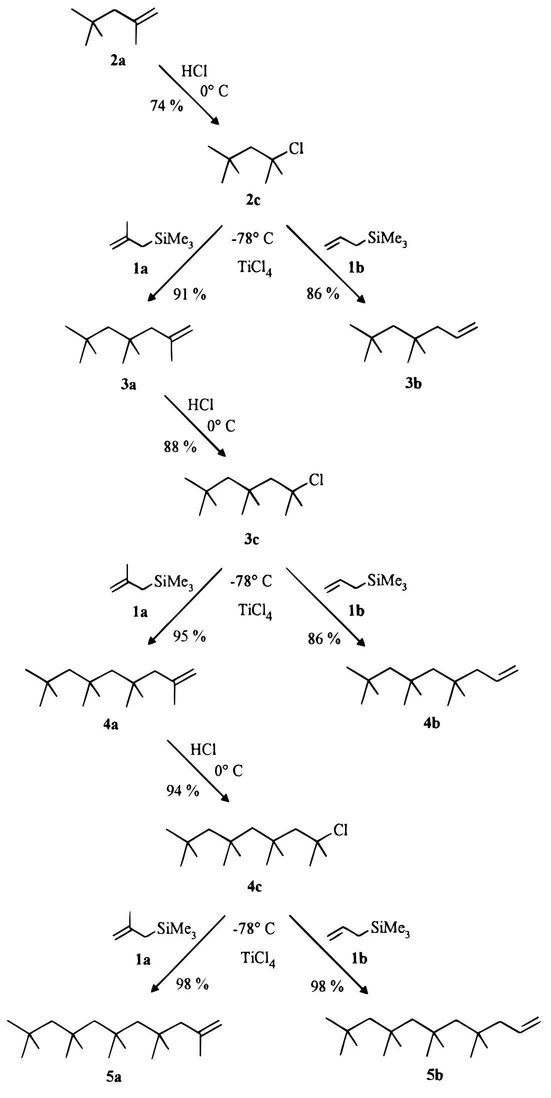


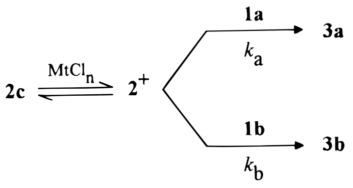
Figure 1. Changeover from constant selectivity relationships to the reactivity selectivity principle (Fc = ferrocenyl, Fur = 2,3-dihydrobenzofuran-5-yl). Directly measured rate constants are marked by dots, and results from competition experiments by shaded bars.[12]

Scheme 2



tion 2^+. When variable mixtures of **1a** and **1b** were treated with the tertiary alkyl chloride **2c** and a Lewis

Scheme 3



acid, different ratios of **3a** and **3b** were obtained, which allowed the calculation of k_a/k_b according to eq 1.[20-22]

$$\frac{k_a}{k_b} = \frac{\log\left(1 - \frac{[\mathbf{2c}]_0 R}{[\mathbf{1a}]_0 (R + 1)}\right)}{\log\left(1 - \frac{[\mathbf{2c}]_0}{[\mathbf{1b}]_0 (R + 1)}\right)} \quad \text{with } R = \frac{[\mathbf{3a}]}{[\mathbf{3b}]} \tag{1}$$

Because seven experiments with variable ratios of [**1a**]/[**1b**]/[$TiCl_4$] and six experiments with variable ratios of [**1a**]/[**1b**]/[$AlCl_3$] gave almost identical competition constants, $k_a/k_b = 2.42 \pm 0.26$ and 2.39 ± 0.26, respectively (Table 1), we conclude that the relative reactivities of the allylsilanes do not depend on the nature of the Lewis acid.

An analogous competition experiment as described in Scheme 3 for 2^+ has also been performed for 3^+. As expected, the $AlCl_3$-catalyzed reaction of the higher homologue **3c** with the couple **1a**/**1b** showed a selectivity of $k_a/k_b = 2.47 \pm 0.04$, closely similar to that for cation 2^+ (see above). It is not clear why in this case (**3c** + **1a**/**1b**) the $TiCl_4$-catalyzed reaction gave rise to a slightly lower selectivity ($k_a/k_b = 1.93 \pm 0.07$, Table 2).

The method used to determine the relative reactivities of isobutylene (**1c**) and allylsilane **1b** is illustrated in Scheme 4. Treatment of **2c** with a Lewis acid yields the tertiary carbenium ion 2^+, which either reacts with the allylsilane **1b** to give the termination product **3b** or reacts with isobutylene (**1c**) to yield the homologous carbenium ion 3^+. This cation again selects between **1b** and **1c**, i.e., between termination and propagation, to give **4b** or 4^+.

Table 1. Determination of the Relative Reactivities of 2-Methallyltrimethylsilane (1a) and Allyltrimethylsilane (1b) toward the Tertiary Carbenium Ion 2^+ (CH_2Cl_2, −78 °C)

$[\mathbf{1a}]_0/[\mathbf{1b}]_0$	$[\mathbf{1a}]_0/[\mathbf{2c}]_0$	$[\mathbf{1b}]_0/[\mathbf{2c}]_0$	$MtCl_n$	$[\mathbf{3a}]/[\mathbf{3b}]$	k_a/k_b[a]
1.01	4.96	4.92	$TiCl_4$	2.48	2.58
2.02	11.0	5.47	$TiCl_4$	5.36	2.72
1.81	10.4	5.74	$TiCl_4$	4.87	2.76
1.09	8.06	7.37	$AlCl_3$	2.72	2.56
1.64	12.0	7.35	$AlCl_3$	4.38	2.74
0.99	4.11	4.16	$TiCl_4$	2.04	2.16
0.52	3.00	5.78	$TiCl_4$	1.01	2.04
2.07	7.75	3.74	$TiCl_4$	4.72	2.35
0.84	3.07	3.64	$AlCl_3$	1.62	2.03
0.93	3.40	3.66	$AlCl_3$	1.97	2.25
2.12	7.73	3.64	$TiCl_4$	4.79	2.33
0.47	4.06	8.60	$AlCl_3$	1.17	2.59
0.71	2.52	3.56	$AlCl_3$	1.43	2.16

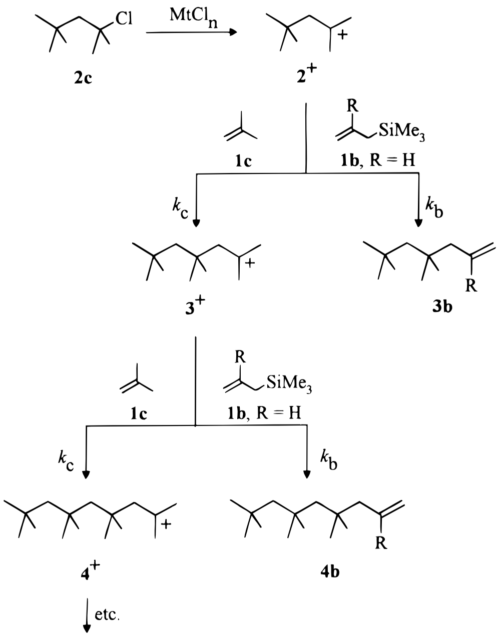
[a] From eq 1; $k_a/k_b(TiCl_4) = 2.42 \pm 0.26$; $k_a/k_b(AlCl_3) = 2.39 \pm 0.26$.

Table 2. Determination of the Relative Reactivities of 2-Methallyltrimethylsilane (1a) and Allyltrimethylsilane (1b) toward the Tertiary Carbenium Ion 3^+ (CH_2Cl_2, −78 °C)

$[\mathbf{1a}]_0/[\mathbf{1b}]_0$	$[\mathbf{1a}]_0/[\mathbf{3c}]_0$	$[\mathbf{1b}]_0/[\mathbf{3c}]_0$	$MtCl_n$	$[\mathbf{4a}]/[\mathbf{4b}]$	k_a/k_b[a]
0.50	4.50	8.96	$TiCl_4$	0.93	1.90
0.40	3.88	9.73	$TiCl_4$	0.72	1.85
0.49	3.63	7.33	$TiCl_4$	0.91	1.90
1.69	6.89	4.07	$TiCl_4$	3.22	1.96
1.00	5.40	5.38	$TiCl_4$	1.99	2.05
0.45	3.88	8.53	$TiCl_4$	0.81	1.83
0.45	3.47	7.79	$TiCl_4$	0.86	2.00
1.00	4.94	4.95	$AlCl_3$	2.36	2.47
0.50	3.95	7.85	$AlCl_3$	1.21	2.51
0.49	4.37	8.87	$AlCl_3$	1.17	2.47
1.02	7.86	7.72	$AlCl_3$	2.39	2.41

[a] From eq 1; $k_a/k_b(TiCl_4) = 1.93 \pm 0.07$; $k_a/k_b(AlCl_3) = 2.47 \pm 0.04$.

Scheme 4



Eventual combination of the cations $\mathbf{3}^+$ and $\mathbf{4}^+$ with Cl^- producing intermediate tertiary chlorides is possible, but this is a reversible process and does not affect our analysis, which is based on the reactivity ratio k_b/k_c. Since the quantity of $\mathbf{3}^+$ produced by the reaction of $\mathbf{2}^+$ with isobutylene (**1c**) finally yields any of the higher adducts (**4b**, **5b**, **6b**, etc.), eq 2 can be derived if the concentrations of **1b** and **1c** remain nearly constant during the reaction ($[\mathbf{1b}] \approx [\mathbf{1b}]_0$; $[\mathbf{1c}] \approx [\mathbf{1c}]_0$).

$$\frac{k_c[\mathbf{1c}]_0}{k_b[\mathbf{1b}]_0} = \frac{[\mathbf{4b}] + [\mathbf{5b}] + [\mathbf{6b}] + \sum[\text{oligomers}]}{[\mathbf{3b}]} \tag{2}$$

The same analysis for the reaction of $\mathbf{3}^+$ with either isobutylene (**1c**) or allyltrimethylsilane (**1b**) yields eq 3. Since k_a/k_b has been shown to be similar for $\mathbf{2}^+$ and $\mathbf{3}^+$ (see above), the same reactivity ratio of k_c/k_b has also been assumed for the various tertiary carbocations of Scheme 4.

$$\frac{k_c[\mathbf{1c}]_0}{k_b[\mathbf{1b}]_0} = \frac{[\mathbf{5b}] + [\mathbf{6b}] + \sum[\text{oligomers}]}{[\mathbf{4b}]} \tag{3}$$

Transformation of eqs 2 and 3 yields eq 4 and 5, which can be combined to give the relative reactivity of **1b** and **1c** (eq 6).

$$[\mathbf{5b}] + [\mathbf{6b}] + \sum[\text{oligomers}] = [\mathbf{3b}]\frac{k_c[\mathbf{1c}]_0}{k_b[\mathbf{1b}]_0} - [\mathbf{4b}] \tag{4}$$

$$[\mathbf{5b}] + [\mathbf{6b}] + \sum[\text{oligomers}] = [\mathbf{4b}]\frac{k_c[\mathbf{1c}]_0}{k_b[\mathbf{1b}]_0} \tag{5}$$

$$\frac{k_b}{k_c} = \left(\frac{[\mathbf{3b}]}{[\mathbf{4b}]} - 1\right)\frac{[\mathbf{1c}]_0}{[\mathbf{1b}]_0} \tag{6}$$

Ten experiments with $TiCl_4$, $GaCl_3$, and $AlCl_3$ as Lewis acids gave a reactivity ratio of $k_b/k_c = 2.18 \pm 0.21$ (Table 3), again independent of the nature of the Lewis acid. In order to exclude that uncontrolled side reactions disturb our evaluation, in some experiments the absolute quantities of **3b** and **4b** were determined by using an internal standard for the gas chromatographic analysis of the product mixtures. The ratios k_b/k_c can then directly be derived from eqs 2 and 3 when the reactants **2c** or **3c** are quantitatively consumed (i.e., $[\mathbf{4b}] + [\mathbf{5b}] + [\mathbf{6b}] + \Sigma[\text{oligomers}] = [\mathbf{2c}]_0 - [\mathbf{3b}]$, eq 2; $[\mathbf{5b}] + [\mathbf{6b}] + \Sigma[\text{oligomers}] = [\mathbf{2c}]_0 - ([\mathbf{3b}] + [\mathbf{4b}])$, eq 3). As shown in Table 3, the reactivity ratios obtained in this way agreed with k_b/k_c obtained by evaluating eq 6.

The reliability of this method was examined by performing a similar series of experiments with the couple 2-methallyltrimethylsilane (**1a**) and isobutylene (**1c**) that yielded a reactivity ratio of $k_a/k_c = 7.10 \pm 1.28$ (Scheme 4, R = CH_3; Table 4). Error propagation becomes important, however, when k_a/k_c is derived from eq 3, which is seen by the high scatter of the values in the last column of Table 4.

Discussion

Direct rate measurements for the reactions of laser flash photolytically generated benzhydryl cations with highly reactive π-nucleophiles indicated a value of $k = (2-4) \times 10^9$ L mol^{-1} s^{-1} for diffusion control.[27] It is reasonable, therefore, also to assume $k_a = (3 \pm 1) \times 10^9$ L mol^{-1} s^{-1} for the diffusion-controlled reaction of $\mathbf{2}^+$ with **1a**.[12] Combination of this value with the rate ratios k_a/k_b and k_b/k_c determined in this work yields the rate constants for the reactions of $\mathbf{2}^+$ (and $\mathbf{3}^+$) with the allylsilane **1b** and isobutylene (**1c**) (Scheme 5). Since the major uncertainty of this approach is the estimate of the rate constant for diffusion control, the errors

Table 3. Determination of the Relative Reactivities of Allyltrimethylsilane (1b) and Isobutylene (1c) toward the Tertiary Carbenium Ions 2^+ and 3^+ (CH_2Cl_2, −78 °C)

$[\mathbf{1c}]_0/[\mathbf{1b}]_0$	$[\mathbf{1c}]_0/[\mathbf{2c}]_0$	$[\mathbf{1b}]_0/[\mathbf{2c}]_0$	$MtCl_n$	$[\mathbf{3b}]/[\mathbf{4b}]$	k_b/k_c[a]	k_b/k_c[b]	k_b/k_c[c]
2.25	15.2	6.75	$TiCl_4$	1.800	1.80		
2.17	28.5	13.1	$TiCl_4$	1.827	1.79		
4.65	40.8	8.77	$TiCl_4$	1.514	2.39		
3.69	32.8	8.89	$GaCl_3$	1.623	2.30		
5.07	35.7	7.04	$AlCl_3$	1.486	2.46		
4.23	44.0	10.4	$TiCl_4$	1.527	2.23		
4.15	32.4	7.81	$TiCl_4$	1.555	2.30	2.18	2.13
2.23	24.4	10.9	$TiCl_4$	1.977	2.18	2.06	1.96
4.52	25.9	5.72	$TiCl_4$	1.473	2.14	2.54	2.82
4.90	41.9	8.55	$TiCl_4$	1.446	2.19	2.42	2.56
					2.18 ± 0.21	2.30 ± 0.19	2.37 ± 0.34

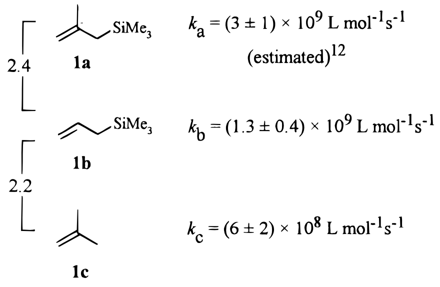
[a] From eq 6. [b] From eq 2, determination of [**3b**] with internal standard, assuming $[\mathbf{4b}] + [\mathbf{5b}] + [\mathbf{6b}] + \Sigma[\text{oligomers}] = [\mathbf{2c}]_0 - [\mathbf{3b}]$. [c] From eq 3, determination of [**3b**] and [**4b**] with internal standard, assuming $[\mathbf{5b}] + [\mathbf{6b}] + \Sigma[\text{oligomers}] = [\mathbf{2c}]_0 - ([\mathbf{3b}] + [\mathbf{4b}])$.

Table 4. Determination of the Relative Reactivities of 2-Methallyltrimethylsilane (1a) and Isobutylene (1c) toward the Tertiary Carbenium Ions 2^+ and 3^+ (CH_2Cl_2, −78 °C)

$[\mathbf{1c}]_0/[\mathbf{1a}]_0$	$[\mathbf{1c}]_0/[\mathbf{2c}]_0$	$[\mathbf{1a}]_0/[\mathbf{2c}]_0$	$MtCl_n$	$[\mathbf{3a}]/[\mathbf{4a}]$	k_a/k_c[a]	k_a/k_c[b]	k_a/k_c[c]
3.09	17.7	5.74	$TiCl_4$	2.547	4.77		
4.44	29.1	6.54	$TiCl_4$	2.160	5.15		
4.11	36.9	8.98	$TiCl_4$	2.880	7.72		
6.53	50.0	7.66	$TiCl_4$	2.373	8.96		
5.17	33.0	6.37	$TiCl_4$	2.053	5.45		
4.39	41.4	9.44	$TiCl_4$	2.893	8.30		
6.22	31.8	5.11	$TiCl_4$	2.120	6.97	7.28	7.72
7.39	34.7	4.70	$GaCl_3$	2.133	8.38	5.68	4.28
7.42	27.6	3.72	$AlCl_3$	2.027	7.62	7.15	6.65
6.39	25.5	3.99	$AlCl_3$	2.213	7.75	4.21	2.72
6.38	27.9	4.37	$AlCl_3$	2.147	7.32	4.69	3.36
5.30	20.1	3.79	$AlCl_3$	2.280	6.79	4.28	2.82
					7.10 ± 1.28	5.55 ± 1.27	4.59 ± 1.92

[a] From eq 6. [b] From eq 2, determination of [**3a**] with internal standard, assuming $[\mathbf{4a}] + [\mathbf{5a}] + [\mathbf{6a}] + \Sigma[\text{oligomers}] = [\mathbf{2c}]_0 - [\mathbf{3a}]$. [c] From eq 3, determination of [**3a**] and [**4a**] with internal standard, assuming $[\mathbf{5a}] + [\mathbf{6a}] + \Sigma[\text{oligomers}] = [\mathbf{2c}]_0 - ([\mathbf{3a}] + [\mathbf{4a}])$.

Scheme 5



introduced by the uncertainties of the relative reactivities are negligible.[23]

Because 2^+ (or 3^+) represents a model for the active chain end in carbocationic isobutylene polymerization, k_c given in Scheme 5 corresponds to the propagation rate constant of this oligomerization. Since fast bimolecular reactions do not have an enthalpic barrier,[24] this rate constant can be expected to be indepenent of temperature. Comparison with literature data shows a good agreement between k_c and the propagation rate constant determined by Taylor for the bulk polymerization of isobutylene initiated by ionizing irradiation.[6] It should be noted, however, that bulk polymerizations may follow a different mechanism[25] and that these data may not be directly comparable.

The order of magnitude of the propagation rate constant reported in this work is consistent with the results of direct rate measurements for reactions of isobutylene with benzhydryl cations. Figure 2 shows that a rate constant of 3.67×10^3 L mol^{-1} s^{-1} is already found for the reaction of isobutylene with the highly stabilized bis(*p*-tolyl)carbenium ion.[26] Furthermore, a rate constant of 9.8×10^6 L mol^{-1} s^{-1} has been determined for the reaction of 2-methyl-1-pentene (a structural analogue of isobutylene) with the bis(*p*-chlorophenyl)carbenium ion.[27] Since tertiary alkyl cations (e.g., 2^+ and 3^+) are less stabilized than these benzhydryl cations according to their ionization rates in solvolysis reactions, their reactivity toward isobutylene must be higher.

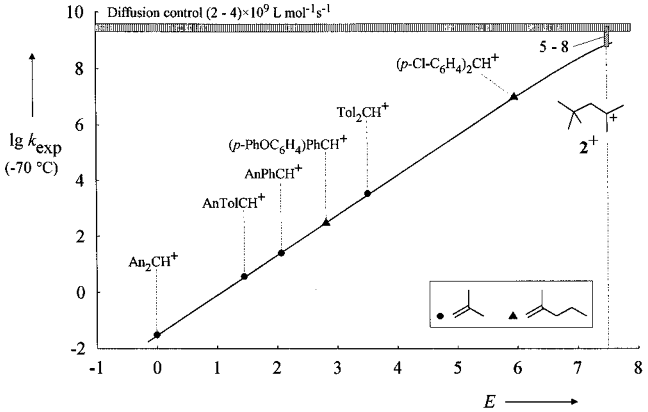


Figure 2. Directly measured rate constants for the reactions of benzhydryl cations with isobutylene (**1c**) or 2-methyl-1-pentene (CH_2Cl_2, −70 °C) (An = *p*-$MeOC_6H_4$, Tol = *p*-MeC_6H_4; rate constants from refs 9, 10, and 26−28; *E* values from refs 11 and 12).

The rate constant determined for the attack of tertiary alkyl cations at isobutylene in this work, i.e., the propagation rate constant in carbocationic isobutylene polymerization, is, therefore, in perfect agreement with the large set of directly measured rate constants for the reactions of other types of carbocations with alkenes.[9,10,26,28]

The method of determination of propagation rate constants in carbocationic homopolymerizations introduced in this article should also be applicable to other monomers, such as styrenes and vinyl ethers. Since it is based on the selectivity of carbocations which are generated from suitable precursors by chemical ionization, this method does not depend on the presence of certain chromophores as in the case of flash photolytic generation of carbocations. It does not require any special apparatus because detection of the reaction products can be carried out chromatographically. Finally, it is an important advantage of this method that incomplete ionization cannot affect the results as only reactivity ratios are determined which are characteristic for the reactivities of the active propagating species.

It has to be stressed, however, that k_p^+ determined in this way is more than 4 orders of magnitude greater than those values considered to be most reliable by Plesch (Table 12 in ref 1). Since preliminary experiments with styrenes also indicate propagation rate constants considerably larger than those selected by Plesch,[1] a principal discrepancy becomes obvious. In order to resolve it, we have to assume that either the results obtained with low molecular weight model compounds are not relevant for macromolecules or that the presently accepted k_p^+ values correspond to apparent rate constants and have to be corrected.

Experimental Section

Dichloromethane (Merck, p.a.) was stirred over sulfuric acid for 3 days, then washed with water, aqueous $NaHCO_3$ solution, and again with water, dried over $CaCl_2$, and distilled from CaH_2 before use. Titanium tetrachloride (Fluka) was distilled and stored under nitrogen, 2,6-di-*tert*-butylpyridine (Fluka) was distilled from KOH, and aluminum trichloride (Fluka) was stored under argon. Allyltrimethylsilane (Fluka, >99%), isobutylene (Fluka, >99%), gallium trichloride (Aldrich, >99.99%), and *n*-dodecane (Fluka) were used without further purification. The reaction products were purified by bulb-to-bulb distillation (Büchi KGR-50). The reported boiling points correspond to the temperature of the oven. The GC analyses were performed on a Perkin-Elmer Sigma 3 (packed column, 2.5 m, 4 mm, SE30) and a Spectra Physics SP4290 integrator. The mass spectra were determined on a Finnigan MAT 311A spectrometer with a combined EI/FD source (70 eV). The ^{1}H and ^{13}C NMR spectra were obtained on a Bruker WM 300 spectrometer with $CDCl_3$ as solvent and tetramethylsilane (δ = 0.00 ppm) as an internal standard.

2-Methallyltrimethylsilane (1a)[29a] was synthesized as briefly described in ref 29b: In a three-necked flask (1 L) with stirrer, dropping funnel, and thermometer, a solution of methallyl chloride (26.3 g, 290 mmol) in dry THF (200 mL) was added dropwise ($\approx$5 h) to a mixture of Mg turnings (10.7 g, 440 mmol), a piece of iodine, trimethylchlorosilane (28.3 g, 260 mmol), and dry THF (300 mL) at 0 °C with ultrasound irradiation (to avoid coupling products). The beginning of the reaction was detected by consumption of the iodine, i.e., the decolorization of the solution. The mixture was kept at 0 °C for another 5 h (ultrasound) and then stirred at room temperature for 15 h. After hydrolysis with a mixture of aqueous NH_4Cl (300 mL)/NH_3 (100 mL) and separation of the layers, the aqueous layer was extracted with pentane. The combined organic layers were dried over $MgSO_4$ and distilled (109–110 °C/normal pressure) over a packed column to give methallyltrimethylsilane (**1a**) as a colorless liquid of >99% purity (20.0 g, 60%, (Lit.[29a] 109 °C/726 mmHg)); ^{1}H NMR δ = 0.00 (s, 9 H, $SiMe_3$), 1.51 (d, J = 1.0 Hz, 2 H, 1-H), 1.68 (t, J = 1.0 Hz, 3 H, 2-Me), 4.43–4.44 and 4.54–4.56 (2 m, each 1 H, 3-H); ^{13}C NMR δ = −1.4 (q, $SiMe_3$), 25.2 (q, 2-Me), 28.6 (t, C-1), 107.9 (t, C-3), 143.9 (s, C-2).

Hydrochlorination of the Oligoisobutylenes 2a–4a. General Procedure. In a two-necked flask, a solution of the oligoisobutylene in methylene chloride was cooled in an ice bath. After passing gaseous HCl through the solution for 4 h, the organic layer was washed with water and aqueous $NaHCO_3$ solution. The organic fraction was dried over $MgSO_4$, the solvent was evaporated in vacuo, and the residue was distilled.

2-Chloro-2,4,4-trimethylpentane (2c). A solution of **2a** (56.1 g, 0.500 mol) in CH_2Cl_2 (200 mL) was treated with HCl for 4 h. After washing with water (60 mL) and aqueous $NaHCO_3$ solution (60 mL), the product was distilled (52–53 °C/41 mbar) to yield **2c** as a colorless liquid (55.0 g, 74% (Lit.[30] 44 °C/16 mmHg)); ^{1}H NMR δ = 1.05 (s, 9 H, ^{t}Bu), 1.66 (s, 6 H, 1-H), 1.87 (s, 2 H, 3-H); ^{13}C NMR δ = 31.4 (q, C-5), 32.4 (s, C-4), 34.6, (q, C-1), 57.9 (t, C-3), 71.6 (s, C-2); MS *m/z* (%) 113 (1.3, $M^+ - Cl$), 112 (4.5), 97 (22), 77 (13), 57 (100), 56 (58), 55 (23), 41 (58).

2-Chloro-2,4,4,6,6-pentamethylheptane (3c). A solution of **3a** (2.67 g, 15.9 mmol) in CH_2Cl_2 (50 mL) was treated with HCl for 4 h. After washing with water (20 mL) and aqueous $NaHCO_3$ solution (20 mL), the chloro compound was distilled (40–45 °C/1 × 10^{-1} mbar) to yield **3c** as a colorless liquid (2.85 g, 88%); ^{1}H NMR δ = 1.00 (s, 9 H, ^{t}Bu), 1.15 (s, 6 H, 4-Me), 1.39 (s, 2 H, 5-H), 1.68 (s, 6 H, 1-H), 1.96 (s, 2 H, 3-H); ^{13}C NMR δ = 29.9, 35.2 (2 q, C-1, 4-Me), 32.3 (q, C-7), 32.5, 37.3 (2 s, C-4, C-6), 57.1, 58.3 (2 t, C-3, C-5), 71.7 (s, C-2); MS *m/z* (%) 169 (0.5, $M^+ - Cl$), 168 (1.2), 113 (7.6), 97 (31), 73 (10), 57 (100), 56 (8.6), 55 (21), 41 (28). Anal. Calcd for $C_{12}H_{25}Cl$ (204.78): C, 70.38; H, 12.30. Found: C, 69.07; H, 12.37.

2-Chloro-2,4,4,6,6,8,8-heptamethylnonane (4c). A solution of **4a** (0.470 g, 2.09 mmol) in CH_2Cl_2 (20 mL) was treated with HCl for 4 h. After washing with water (10 mL) and aqueous $NaHCO_3$ solution (10 mL), the reaction product was distilled (55–60 °C/2 × 10^{-3} mbar) to yield **4c** as a colorless liquid (0.51 g, 93%); ^{1}H NMR δ = 0.94 (s, 9 H, ^{t}Bu), 1.05 and 1.11 (2 s, each 6 H, 4-Me, 6-Me), 1.28 and 1.42 (2 s, each 2 H, 5-H, 7-H), 1.64 (s, 6 H, 1-H), 1.91 (s, 2 H, 3-H); ^{13}C NMR δ = 30.2, 30.7, 32.4, 35.2 (4 q, C-1, 4-Me, 6-Me, C-9), 32.6, 37.6, 37.7 (3 s, C-4, C-6, C-8), 57.6, 58.2 (2 t, C-3, C-5), 59.0 (t, C-7), 72.1 (s, C-2).

Reaction of the Alkyl Chlorides 2c–4c with the Allylsilanes 1a and 1b. General Procedure. The chloro compound and the allylsilane were dissolved in dry methylene chloride. After cooling in a dry ice bath, the Lewis acid was added slowly and the reaction mixture was stirred for 4–5 h at −78 °C. Aqueous ammonia (30 mL) was added and the mixture was filtered over Celite. The aqueous layer was extracted with CH_2Cl_2, the combined organic fractions were dried over $MgSO_4$, after filtration the solvent was removed, and the reaction products were distilled in vacuo.

4,4,6,6-Tetramethyl-1-heptene (3b). Compounds **2c** (0.30 g, 2.0 mmol) and **1b** (0.68 g, 6.0 mmol) in CH_2Cl_2 (90 mL) were mixed with a $TiCl_4$ solution (0.25 M) in CH_2Cl_2 (4.0 mL, 1.0 mmol). Distillation (75–78 °C/18 mbar) yielded **3b** as a colorless oil (265 mg, 86% (Lit.[17] 162 °C/750 mmHg, 70%)); ^{1}H NMR[17] δ = 0.96 (s, 6 H, 4-Me), 0.98 (s, 9 H, ^{t}Bu), 1.25 (s, 2 H, 5-H), 2.00 (br d, J = 7.4 Hz, 2 H, 3-H), 4.94–5.03 (m, 2 H, 1-H), 5.76–5.90 (m, 1 H, 2-H); ^{13}C NMR δ = 28.8 (q, 4-Me), 32.2 (q, C-7), 32.4, 35.2 (2 s, C-4, C-6), 49.6, 54.4 (2 t, C-3, C-5), 116.7 (t, C-1), 136.2 (d, C-2); MS *m/z* (%) 154 (0.3, M^+), 113 (12), 83 (12), 57 (100), 55 (18), 41 (26). Anal. Calcd for $C_{11}H_{22}$ (154.29): C, 85.63; H, 14.37. Found: C, 85.10; H, 14.38.

2,4,4,6,6-Pentamethyl-1-heptene (3a). Compounds **2c** (0.30 g, 2.0 mmol) and **1a** (0.77 g, 6.0 mmol) in CH_2Cl_2 (90 mL) were mixed with a $TiCl_4$ solution (0.25 M) in CH_2Cl_2 (2.0 mL, 0.50 mmol). Distillation (85–88 °C/19 mbar) yielded **3a** as a colorless oil (305 mg, 91% (Lit.[31] 99 °C/50 mmHg)); ^{1}H NMR δ = 0.95 (s, 9 H, ^{t}Bu), 0.96 (s, 6 H, 4-Me), 1.25 (s, 2 H, 5-H), 1.74 (br s, 3 H, 2-Me), 1.95 (s, 2 H, 3-H), 4.59 and 4.79–4.82 (2 m, each 1 H, 1-H); ^{13}C NMR δ = 25.8 (q, 2-Me), 29.1 (q, 4-Me), 32.3 (q, C-7), 32.4, 35.9 (2 s, C-4, C-6), 53.0, 55.7 (2 t, C-3, C-5), 114.4 (t, C-1), 144.0 (s, C-2); MS *m/z* (%) 169, 168

(0.2, 0.5, M$^+$ + 1, M$^+$), 113 (11), 97 (12), 57 (100), 55 (18), 41 (26). Anal. Calcd for $C_{12}H_{24}$ (168.32): C, 85.63; H, 14.37. Found: C, 85.32; H, 14.74.

4,4,6,6,8,8-Hexamethyl-1-nonene (4b). Compounds **3c** (0.31 g, 1.5 mmol) and **1b** (0.51 g, 4.5 mmol) in CH_2Cl_2 (50 mL) were mixed with a $TiCl_4$ solution (0.38 M) in CH_2Cl_2 (1.0 mL, 0.38 mmol). Distillation (40−45 °C/1 × 10^{-1} mbar) yielded **4b** as a colorless oil (0.27 g, 86%); ^{1}H NMR $\delta = 0.98$ (s, 15 H, Me), 1.07 (s, 6 H, Me), 1.32 (s, 4 H, 5-H, 7-H), 2.00 (dt, 2 H, $J_d = 7.4$ Hz, $J_t = 1.1$ Hz, 3-H), 4.93−5.03 (m, 2 H, 1-H), 5.76−5.90 (m, 1 H, 2-H); ^{13}C NMR $\delta = 29.1$, 30.9 (2 q, 4-Me, 6-Me), 32.4 (q, C-9), 32.5, 35.3, 37.5 (3 s, C-4, C-6, C-8), 50.3, 55.1 (2 t, C-3, C-5), 58.0 (t, C-7), 116.7 (t, C-1), 136.1 (d, C-2); MS *m/z* (%) 210 (0.3, M$^+$), 169 (1.2), 113 (24), 83 (26), 57 (100), 55 (20), 41 (17). Anal. Calcd for $C_{15}H_{30}$ (210.40): C, 85.63; H, 14.37. Found: C, 84.86; H, 14.38.

2,4,4,6,6,8,8-Heptamethyl-1-nonene (4a). Compounds **3c** (0.31 g, 1.5 mmol) and **1a** (0.58 g, 4.5 mmol) in CH_2Cl_2 (50 mL) were mixed with a $TiCl_4$ solution (0.38 M) in CH_2Cl_2 (1.0 mL, 0.38 mmol). Distillation (50−58 °C/1 × 10^{-1} mbar) yielded **4a** as a colorless oil (320 mg, 95%); ^{1}H NMR $\delta = 0.99$ (s, 9 H, ^{t}Bu), 1.02 and 1.09 (2 s, each 6 H, 4-Me, 6-Me), 1.33 and 1.37 (2 s, each 2 H, 5-H, 7-H), 1.78 (m$_c$, 3 H, 2-Me), 2.00 (br s, 2 H, 3-H), 4.63−4.64 and 4.83−4.86 (2 m, each 1 H, 1-H); ^{13}C NMR $\delta = 25.8$ (q, 2-Me), 29.4, 30.7 (2 q, 4-Me, 6-Me), 32.5 (q, C-9), 32.6, 36.2, 37.7 (3 s, C-4, C-6, C-8), 53.8, 56.4 (2 t, C-3, C-5), 58.2 (t, C-7), 114.4 (t, C-1), 143.9 (s, C-2); MS *m/z* (%) 224 (0.3, M$^+$), 169 (1.2), 113 (27), 97 (17), 83 (7.0), 57 (100), 55 (19), 41 (15). Anal. Calcd for $C_{16}H_{32}$ (224.43): C, 85.63; H, 14.37. Found: C, 85.15; H, 14.40.

4,4,6,6,8,8,10,10-Octamethyl-1-undecene (5b). Compounds **4c** (0.200 g, 0.766 mmol) and **1b** (0.53 g, 4.6 mmol) in CH_2Cl_2 (15 mL) were mixed with $TiCl_4$ (0.20 mL, 1.8 mmol). Distillation (65−75 °C/2 × 10^{-3} mbar) yielded **5b** as a colorless oil (200 mg, 98%); ^{1}H NMR $\delta = 0.86$ (s, 15 H, Me), 0.96 and 0.97 (2 s, each 6 H, Me), 1.20 (s, 4 H, CH_2), 1.27 (s, 2 H, CH_2), 1.88 (d, 2 H, $J = 7.4$ Hz, 3-H), 4.82−4.92 (m, 2 H, 1-H), 5.64−5.78 (m, 1 H, 2-H); ^{13}C NMR $\delta = 29.1$, 30.7, 30.9 (3 q, 4-Me, 6-Me, 8-Me), 32.4 (q, C-11), 32.6, 35.4, 37.7 (3 s, C-4, C-6, C-8, C-10), 50.4, 55.6 (2 t, C-3, C-5), 58.1, 58.7 (2 t, C-7, C-9), 116.7 (t, C-1), 136.1 (d, C-2); MS *m/z* (%) 170 (0.4, M$^+$ − C_7H_{12}), 130 (8), 114 (35), 97 (14), 84 (41), 57 (100), 55 (30), 42 (32).

2,4,4,6,6,8,8,10,10-Nonamethyl-1-undecene (5a). Compounds **4c** (0.260 g, 1.00 mmol) and **1a** (0.770 g, 6.00 mmol) in CH_2Cl_2 (15 mL) were mixed with $TiCl_4$ (0.30 mL, 2.7 mmol). Distillation (75−85 °C/2 × 10^{-3} mbar) yielded **5a** as a colorless oil (275 mg, 98%); ^{1}H NMR $\delta = 0.95$ (s, 9 H, ^{t}Bu), 0.99, 1.05, 1.06 (3 s, each 6 H, 4-Me, 6-Me, 8-Me), 1.29, 1.34, 1.37 (3 s, each 2 H, 5-H, 7-H, 9-H), 1.74 (d, $J = 1.1$ Hz, 3 H, 2-Me), 1.96 (br s, 2 H, 3-H), 4.60−4.61 and 4.80−4.83 (2 m, each 1 H, 1-H); ^{13}C NMR $\delta = 25.7$ (q, 2-Me), 29.4, 30.7, 31.0 (3 q, 4-Me, 6-Me, 8-Me), 32.4 (q, C-11), 32.6, 36.2, 37.7, 37.8 (4 s, C-4, C-6, C-8, C-10), 53.8, 56.8 (2 t, C-3, C-5), 58.2, 58.7 (2 t, C-7, C-9), 114.4 (t, C-1), 143.9 (s, C-2); MS *m/z* (%) 225 (0.3, M$^+$ − C_4H_7), 174 (7.9), 129 (31), 113 (47), 97 (30), 57 (100), 55 (34), 41 (28).

Competition Experiments. General Procedure. The alkyl chloride **2c** or **3c** and the nucleophiles (**1a**, **1b**, **1c**) were dissolved in dry CH_2Cl_2 and cooled in a dry ice bath (isobutylene was condensed into the precooled solution). In some of the oligomerization experiments, *n*-dodecane (150 μL, internal standard) and 2,6-di-*tert*-butylpyridine (5 μL, proton trap) were added. The reaction was started at −78 °C by adding the appropriate Lewis acid. After 30−40 min, the reaction mixture was hydrolyzed with aqueous ammonia (20 mL), and the organic layer was dried over $MgSO_4$ and analyzed by GC without further purification. The response factors for evaluation of the gas chromatographic analysis are based on the relative ratios of carbon atoms.[32]

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Supporting Information Available: Tables containing concentrations of the reactants and products in the competition experiments (3 pages). Ordering information is given on any current masthead page.

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