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Determination of the Absolute Rate Constants of Propagation for Ion Pairs and Free Ions in the Living Cationic Polymerization of Isobutylene[†]

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Introduction

In contrast to the great technical and academic importance of cationic polymerization, the detailed understanding of polymerization kinetics is rather incomplete. For most cationic polymerization reactions, individual rate constants, especially those concerning the propagation (k_p), are not precisely known and are still a topic of substantial controversy.[1] According to the classical picture of binary ionogenic equilibria, cationic propagation may involve free ions and ion pairs. Under common conditions, however, ion pair dissociation may be suppressed by counteranions of onium ions formed in the reaction of adventitious protons with added Lewis bases, e.g., proton traps in the presence of Lewis acid. Capping of cation with diarylethylenes and 2-alkyl(or aryl)furans also results in the formation of common anions since the capped species are fully ionized, and the equilibrium constant of dissociation $K_d \sim 10^{-4}$ mol L^{-1}. Therefore, recently reported kinetic studies yielded the absolute rate constants of propagation for ion pairs ($k_p^{\pm}$) in the living carbocationic polymerization of isobutylene (IB),[2,3] styrene (St),[4] *p*-methoxystyrene (*p*-MeOSt),[5] *p*-chlorostyrene (*p*-ClSt),[6] 2,4,6-trimethylstyrene (TMeSt),[7] and *p*-methylstyrene (*p*-MeSt)[8] determined by two different reaction clock methods: competition experiments and/or kinetic studies of diffusion-limited addition of π-nucleophiles by on-line UV−vis spectroscopy.

In the absence of common ion sources propagation may involve at least two species: free ions and ion pairs at concentrations determined by K_d and the total concentration of cations. While it is generally believed that carbenium ions are 5−20 times more reactive than ion pairs,[9] studies with benzhydryl cations indicated[10] identical reactivity of paired and unpaired cations. It was of interest to extend our study of k_p to understand the reactivity of ion pairs and free ions in the living carbocationic polymerization of IB.

As we reported before,[2] competition experiments are suitable for the determination of both the absolute rate constants of propagation for ion pairs ($k_p^{\pm}$) and the absolute rate constants of propagation for free ions (k_p^{+}). In the exclusive presence of ion pairs or free ions, competition yields $k_p^{\pm}$ or k_p^{+}, respectively. When capping results in stable carbenium ions in the competition reaction, the formation of common anion suppresses ion pair dissociation, and as discussed above, the concentration of free ions will be negligible compared to that of the paired ions. Under these conditions even in the absence of Lewis bases competition yields $k_p^{\pm}$. Competition experiments, however, could also be carried out with nucleophiles, e.g., silanes and stannanes, that react with carbocations with diffusion-limited rates and do not produce stable carbenium ions. Roth and Mayr have already utilized allylsilanes to determine propagation rate constant for the carbocationic oligomerization of IB in dichloromethane.[11] Under high-purity conditions in the absence of added proton trap, these experiments should yield k_p^{+} since the $K_i \sim 10^{-7}$ mol L^{-1} reported earlier[2,3] suggests extremely low cation concentration (less than 1×10^{-12} mol L^{-1}). In this Note, results of competition experiments using allyltrimethylsilane and methallyltrimethylsilane as capping agent are reported to determine $k_p^{\pm}$ and k_p^{+}.

Experimental Section

Materials. For the determination of $k_p^{\pm}$, methyl chloride (MeCl) and isobutylene (IB) were dried in the gaseous state by passing them through in-line gas-purifier columns packed with BaO/Drierite. They were condensed at −80 °C in the cold bath of a glovebox prior to polymerization. Titanium tetrachloride ($TiCl_4$, Aldrich, 99.9%), 2,6-di-*tert*-butylpyridine (DTBP, Aldrich, 97+%), allyltrimethylsilane (ATMS, Aldrich, 98%), and methallyltrimethylsilane (MTMS, Aldrich, 97%) were used as received. The 2-chloro-2,4,4-trimethylpentane (TMPCl) was synthesized according to the literature.[12] Hexanes (Hex, Doe & Ingals, Technical grade) was refluxed for 60 h with concentrated sulfuric acid. It was washed three times with 10% NaOH and then with distilled water repeatedly until neutral. After drying overnight over anhydrous Na_2SO_4, it was refluxed overnight with calcium hydride (CaH_2) under nitrogen and distilled to a round-bottom flask containing CaH_2. It was again refluxed overnight with CaH_2 under nitrogen and distilled just before use. Methanol (MeOH, Doe & Ingals, Technical grade) was purified by simple distillation.

For the determination of k_p^{+}, MeCl was further distilled from triethylaluminum (Aldrich, 1.9 M in toluene) and was condensed at −80 °C. Isobutylene was further purified from CaH_2 by bulb-to-bulb distillation and condensed at −80 °C. Hexanes and TMPCl were further purified from CaH_2 under high vacuum just prior to use. Allyltrimethylsilane and methallyltrimethylsilane were distilled from CaH_2 under high vacuum just prior to use.[13]

Polymerization. Polymerizations were carried out under a dry nitrogen atmosphere ($[H_2O] < 0.5$ ppm) in an MBraun 150-M glovebox (Innovative Technology Inc., Newburyport, MA). Large (75 mL) culture tubes equipped with Teflon-lined caps were used as polymerization reactors. In all experiments the volume of IB was deducted from that of hexanes; thus, the Hex/MeCl ratio indicates the (Hex + IB)/MeCl ratio. The polymerization temperature was controlled to -80 ± 1 °C. The total volume of the reaction mixture was 25 mL. After a predetermined time polymerization was terminated by the addition of excess prechilled methanol (1.0 mL). Polyisobutylene (PIB) was recovered and purified twice by precipitation from Hex/methanol. Monomer conversions were determined by gravimetric analysis.

In a typical competition experiment the polymerization was carried out using the following concentrations: [TMPCl] = 0.002 mol L^{-1}, [DTBP] = 0.004 mol L^{-1}, [ATMS] = 0.003 mol L^{-1}, [IB] = 1.0 mol L^{-1}, and [$TiCl_4$] = 0.036 mol L^{-1}. Into a 75 mL culture tube at −80 °C 12.3 mL of Hex at room temperature, 9.8 mL of MeCl at −80 °C, 0.4 mL of DTBP stock solution in Hex (0.25 mol L^{-1}) at −80 °C, 0.4 mL of TMPCl stock solution in Hex (0.125 mol L^{-1}) at −80 °C, 1.95 mL of IB at −80 °C, and 1.0 mL of ATMS stock solution in Hex at −80 °C (0.075 mol L^{-1}) were added and mixed thoroughly. The

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[†] This paper is dedicated to Professor Pierre Sigwalt on the occasion of his 80th birthday.

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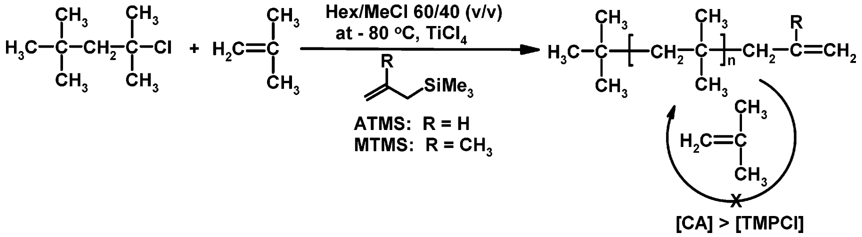
Scheme 1



polymerization was started by the addition of 0.5 mL of $TiCl_4$ solution (1.8 mol L^{-1}, in Hex/MeCl 60/40 (v/v)) at −80 °C. After a predetermined time (2 h) 1.0 mL of prechilled methanol at −80 °C was added to the reaction mixture to quench the polymerization. The polymer was precipitated twice from methanol to obtain 447 mg of PIB polymer (conversion = 31.9%, M_n = 9200, PDI = 1.8).

Characterization. Molecular weights were measured with a Waters HPLC system equipped with a model 510 HPLC pump, model 410 differential refractometer, model 441 absorbance detector, on-line multiangle laser light scattering (MALLS) detector (MiniDawn, Wyatt Technology Inc.), model 712 sample processor, and five Ultrastyragel GPC columns connected in the following series: 500, 10^3, 10^4, 10^5, and 100 Å. Tetrahydrofuran was used as eluent at a flow rate of 1.0 mL/min at room temperature. The measurements were carried out at room temperature. The ^{1}H NMR spectra were obtained on a Bruker 500 MHz spectrometer using $CDCl_3$ as a solvent (Cambridge Isotope Lab., Inc.) and tetramethylsilane (δ_H 0.00) as an internal standard.

Results and Discussions

In the competition experiments polymerizations are carried out in the presence of a capping/trapping agent (nucleophile). The polymerization at well-chosen capping agent concentration stops short of completion when all polymer chain ends are capped, and the capped cationic chain ends do not initiate polymerization of the monomer. In this study allyltrimethylsilane and methallyltrimethylsilane were selected as capping agents based on an earlier report by Roth and Mayr[11] that the addition of MTMS to PIB cation (PIB^+) is diffusion-limited while ATMS adds at 2.4 times lower rate. The competition experiment of IB with ATMS or MTMS as a capping agent (CA) is shown in Scheme 1.

In the competition experiment, the conversion as well as the number-average molecular weight reaches a liming value.[2] From the limiting conversion (x_∞^{IB}) or from the limiting number-average degree of polymerization ($DP_{n,\infty}$) the rate constant ratio k_p/k_c, where k_p is the rate constant of propagation for IB and k_c is the rate constant of addition of the capping agent to PIB^+ cation, can be calculated using eqs 1 and 2.[2] A detailed kinetic treatment of competition experiment is available in ref 2.

$$\frac{k_p}{k_c} = \frac{\ln(1 - x_\infty^{IB})}{\ln(1 - [PIBCl]_0/[CA]_0)} \qquad (1)$$

$$\frac{k_p}{k_c} = \frac{\ln(1 - DP_{n,\infty}[PIBCl]_0/[IB]_0)}{\ln(1 - [PIBCl]_0/[CA]_0)} \qquad (2)$$

In eqs 1 and 2, $[PIBCl]_0$, $[CA]_0$, and $[IB]_0$ are the initial chain end, capping agent, and IB concentration, respectively. In the presence of proton trap DTBP, only ion pairs are considered as active species since ion pair dissociation is suppressed by common anions of the pyridinium salt formed from existing traces of moisture in the presence of Lewis acid, $TiCl_4$. Therefore, in the presence of DTBP competition yields $k_p^{\pm}/k_c^{\pm}$. Alternatively, in the exclusive presence of free ions (in absence of DTBP and under high-purity conditions), competition experiment yields k_p^+/k_c^+. When the capping reaction is diffusion-limited, differentiation between $k_c^{\pm}$ and k_c^+ is unnecessary since $k_c^{\pm} = k_c^+$.

Competition Experiment of IB in the Presence of DTBP: Determination of $k_p^{\pm}$. The competition experiments of IB with ATMS and MTMS were carried out in hexanes/MeCl 60/40 (v/v) solvent mixtures at −80 °C in the presence of DTBP as proton scavenger. First, the time necessary to reach limiting conversion (x_∞^{IB}) was determined at different ATMS and MTMS concentrations. The limiting conversion and limiting number-average degree of polymerization were reached with both ATMS and MTMS (Figure 1). The number-average molecular weight (M_n) of the polymer determined by GPC is close to the calculated value based on the assumption that one living chain is formed from one molecule of initiator. Since competition experiments involve bimolecular termination, the molecular weight distributions of the polymers were close to the most probable distribution ($M_w/M_n \approx 2$). The ^{1}H NMR spectra of the products of competition experiments using ATMS and MTMS as capping agent as a function of time are shown in Figures 2 and 3, respectively. The ^{1}H NMR spectroscopy confirmed the absence of uncapped $-CH_2-C(CH_3)_2-Cl$ ends (absence of CH_2 signal at 1.92 ppm and CH_3 signal at 1.66 ppm). Furthermore, the molecular weights determined by ^{1}H NMR spectroscopy assuming complete capping were similar to the molecular weights determined by GPC, confirming that all chain ends are capped by the corresponding capping agent and side reactions are absent. The reactivity ratio,

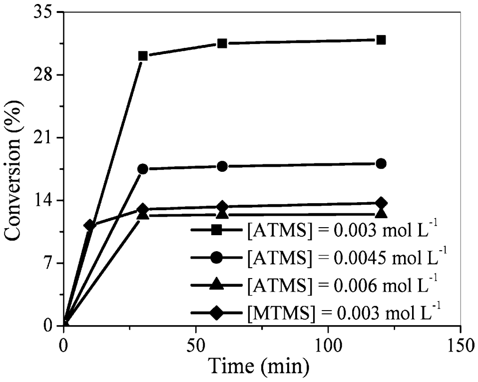


Figure 1. Time vs conversion plot in the competition experiment of IB polymerization with allyltrimethylsilane or methallyltrimethylsilane as capping agent in hexanes/MeCl 60/40 (v/v)at −80 °C using [IB] = 1.0 mol L^{-1}, [TMPCl] = 0.002 mol L^{-1}, [DTBP] = 0.004 mol L^{-1}, and [$TiCl_4$] = 0.036 mol L^{-1} at different capping agent concentrations.

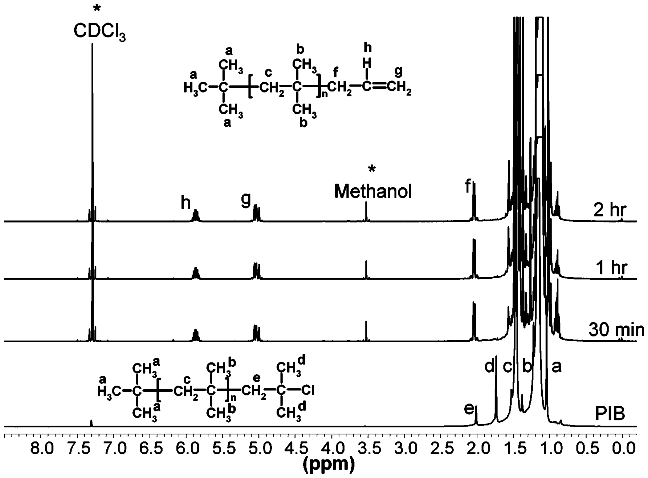


Figure 2. ^{1}H NMR spectra of PIB (PIB-Cl is shown for comparison) and PIB obtained after the competition experiment of IB polymerization with allyltrimethylsilane as capping agent at different times in hexanes/MeCl 60/40 (v/v) at −80 °C using [IB] = 1.0 mol L^{-1}, [TMPCl] = 0.002 mol L^{-1}, [DTBP] = 0.004 mol L^{-1}, [TiCl$_4$] = 0.036 mol L^{-1}, and [ATMS] = 0.006 mol L^{-1}.

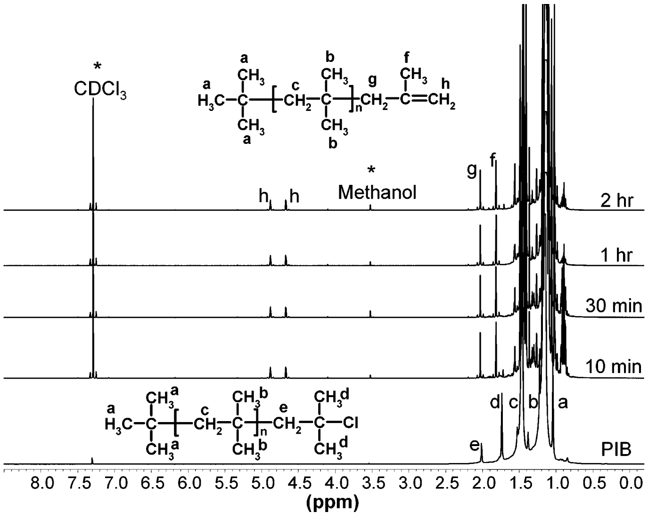


Figure 3. ^{1}H NMR spectra of PIB (PIB-Cl is shown for comparison) and PIB obtained after the competition experiment of IB polymerization with methallyltrimethylsilane as capping agent at different times in hexanes/MeCl 60/40 (v/v) at −80 °C using [IB] = 1.0 mol L^{-1}, [TMPCl] = 0.002 mol L^{-1}, [DTBP] = 0.004 mol L^{-1}, [TiCl$_4$] = 0.036 mol L^{-1}, and [MTMS] = 0.003 mol L^{-1}.

$k_p^{\pm}/k_c^{\pm}$, was calculated from x_∞^{IB} using eq 1 and from the $DP_{n,\infty}$ using eq 2. The two methods yielded similar $k_p^{\pm}/k_c^{\pm}$ values. Detailed results for the competition experiments in the presence of DTBP as proton trap and ATMS or MTMS as capping agent are presented in Table 1.

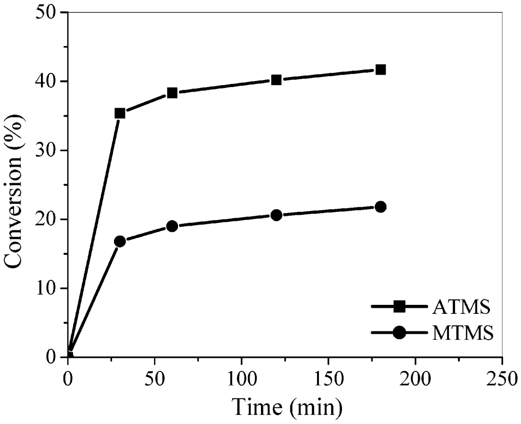


Figure 4. Time vs conversion plot in the competition experiment of IB polymerization in absence of DTBP (under high-purity conditions) with allyltrimethylsilane or methallyltrimethylsilane as capping agent in hexanes/MeCl 60/40 (v/v) at −80 °C using [IB] = 1.0 mol L^{-1}, [TMPCl] = 0.002 mol L^{-1}, [ATMS] = [MTMS] = 0.003 mol L^{-1}, and [TiCl$_4$] = 0.036 mol L^{-1}.

Since the rate of termination is known (for ATMS $k_c^{\pm} = (1.3 \pm 0.4) \times 10^9$ L mol^{-1} s^{-1} and for MTMS $k_c^{\pm} = (3 \pm 1.0) \times 10^9$ L mol^{-1} s^{-1}),[11] the absolute propagation rate constant of ion pairs can be evaluated. The $k_p^{\pm} = (4.2{-}4.7) \times 10^8$ L mol^{-1} s^{-1} values are similar to those reported earlier.[2,3,11]

In the control experiment, i.e., experiments carried out in the absence of initiator TMPCl (direct initiation), and under the same conditions, 1.8% and 0.9% conversions were obtained after 2 h using ATMS and MTMS as capping agent, respectively. Thus, direct initiation is operational during the competition experiment of IB initiated by the TMPCl/TiCl$_4$ initiating system using ATMS and MTMS as capping agent, but it is much slower (practically negligible) than in the presence of initiator and the kinetics of competition reaction is unaffected.

Competition Experiment "Under High-Purity Conditions" in the Absence of DTBP: Determination of k_p^+. To determine k_p^+, similar competition experiments have been carried out with ATMS or MTMS as capping agent in hexanes/MeCl 60/40 (v/v) solvent mixture at −80 °C in the absence of DTBP. The limiting conversion and limiting number-average degree of polymerization were reached with both ATMS and MTMS. Figure 4 shows the conversion vs time plots in the competition experiment of IB polymerization with ATMS and MTMS as capping agents. The M_n of PIB obtained in the competition experiments is similar to the calculated value based on the assumption that one living chain is formed from one molecule of TMPCl. The molecular weight distributions of the products were close to the expected most probable

Table 1. Limiting Conversion, Molecular Weight (M_n), Molecular Weight Distribution (PDI), and Absolute Rate Constants of Propagation for Ion Pairs in the Competition Experiment of Isobutylene (IB) Polymerization with Allyltrimethylsilane or Methallyltrimethylsilane as Capping Agent in Hexanes/MeCl 60/40 (v/v) at −80 °C[a]

[CA] (mol L^{-1})	[DTBP] (mol L^{-1})	x_∞^{IB} (%)	$M_{n,GPC}$	PDI	$M_{n,NMR}$	$k_p^{\pm}/k_c^{\pm}$ (conv)	$k_p^{\pm}/k_c^{\pm}$ (M_n)	$k_p^{\pm} \times 10^{-8}$ (L mol^{-1} s^{-1})
[ATMS] = 0.003	0.004	31.9	9200	1.8	9400	0.350	0.360	4.6
[ATMS] = 0.0045	0.004	18.1	5400	1.9	5500	0.340	0.364	4.6
[ATMS] = 0.006	0.004	12.5	3800	1.9	4100	0.328	0.359	4.5
[ATMS] = 0.003	0.006	32.0	9400	1.9	9300	0.351	0.371	4.7
[MTMS] = 0.003	0.004	13.7	4100	2.0	4300	0.134	0.144	4.2
[MTMS] = 0.003	0.006	13.5	4200	2.1	4500	0.132	0.148	4.2

[a] [TMPCl] = 0.002 mol L^{-1}, [TiCl$_4$] = 0.036 mol L^{-1}, [IB] = 1.0 mol L^{-1}.

Table 2. Limiting Conversion, Molecular Weight (M_n), Molecular Weight Distribution (PDI), and Absolute Rate Constants of Propagation for Free Ions in the Competition Experiment of Isobutylene (IB) Polymerization with Allyltrimethylsilane or Methallyltrimethylsilane as Capping Agent in Hexanes/MeCl 60/40 (v/v) at −80 °C[a]

CA	x_∞^{IB} (%)	$M_{n,GPC}$	PDI	$M_{n,NMR}$	k_p^+/k_c^+ (conv)	k_p^+/k_c^+ (M_n)	$k_p^+ \times 10^{-8}$ (L mol^{-1} s^{-1})
ATMS	40.2	11600	2.1	11900	0.468	0.486	6.2
MTMS	20.6	6100	2.2	5900	0.210	0.223	6.5

[a] [TMPCl] = 0.002 mol L^{-1}, [TiCl$_4$] = 0.036 mol L^{-1}, [IB] = 1.0 mol L^{-1}, [ATMS] = [MTMS] = 0.003 mol L^{-1}; conversion after 2 h was considered as x_∞^{IB}.

distribution ($M_w/M_n \approx 2$). The ^{1}H NMR spectroscopy confirmed the absence of uncapped $-CH_2-C(CH_3)_2-Cl$ chain ends (absence of CH_2 signal at 1.92 ppm and CH_3 signal at 1.66 ppm). The M_ns of the polymers calculated by ^{1}H NMR spectroscopy, assuming one ATMS or MTMS moiety per chain, agreed well with those determined by GPC, suggesting complete capping and the absence of side reactions. The results are presented in Table 2. The reactivity ratios, k_p^+/k_c^+, were calculated from x_∞^{IB} using eq 1 and from DP$_{n,\infty}$ using eq 2 (Table 2.). Since $k_c^\pm = k_c^+$, $k_p^+ = 6.2 \times 10^8$ L mol^{-1} s^{-1} and 6.5×10^8 L mol^{-1} s^{-1} were determined from the competition experiment of IB with ATMS and MTMS as capping agent, respectively. In the absence of DTBP and TMPCl control experiments yielded 6.8% and 4.6% conversions after 2 h using ATMS and MTMS as capping agent, respectively.

For the rate constant of propagation for free ions, a value of 1.5×10^8 L mol^{-1} s^{-1} was obtained by Taylor and Williams for the radiation-induced bulk polymerization of isobutylene under stringent anhydrous conditions.[14] On the basis of the results of Ueno et al.,[15] Plesch, however, calculated a value of 9.1×10^3 L mol^{-1} s^{-1} for the solution polymerization of isobutylene initiated by high-energy radiation in methylene chloride. Recently Williams reevaluated[16] Plesch's derivations and showed that correct analysis of the experimental data of Ueno and co-workers yields $k_p^+ = 1.8 \times 10^8$ L mol^{-1} s^{-1}, similar to the value obtained in bulk. The $k_p^+ = (6.2-6.5) \times 10^8$ L mol^{-1} s^{-1} values determined in the present study for the polymerization of isobutylene in hexanes/MeCl 60/40 (v/v) solvent mixture at −80 °C are in reasonable agreement with the results reported by Williams.

In conclusion, the absolute rate constant of propagation for ion pairs and free ions for the cationic polymerization of isobutylene in hexanes/MeCl 60/40 (v/v) solvent mixture at −80 °C was determined from competition experiments using allyltrimethylsilane or methallyltrimethylsilane as capping agent. Ion pairs and free ions have very similar reactivity, which is consistent with the finding of Mayr's.

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