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Communications to the Editor

Isobutene Polymerization Using Chelating Diboranes: Reactions of a Hindered Pyridine with Carbocations Bearing α-Protons

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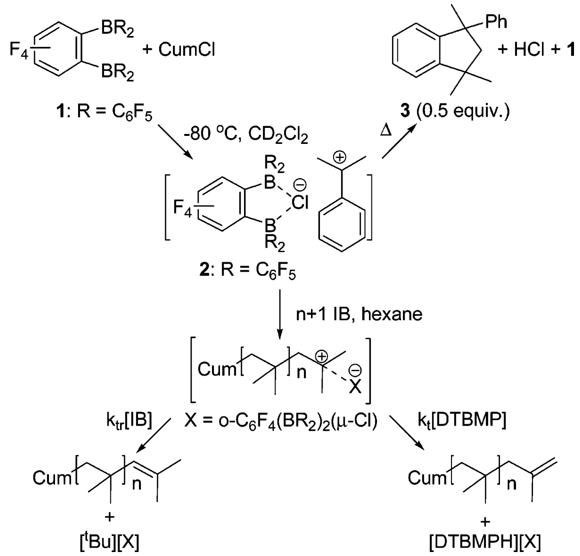
Protic or electrophilic initiators that give rise to weakly coordinating anions (WCA),[1] partnered with propagating carbocations in isobutene (IB) polymerization,[2] is a topic of significant interest in the context of butyl rubber (isobutene−isoprene rubber−IIR) manufacture at elevated T.[3] A variety of initiator systems are effective in neat monomer, hydrocarbon or more polar media,[4] and generally a rather weak T dependence is observed for the MW of poly(isobutene) (PIB) or IIR formed. These polymerizations are uncontrolled with MW values in several cases, comparable to those that can be achieved using γ-ray initiation involving "free" carbocations.[5]

Recently, we communicated that chelating diborane **1** (Scheme 1)[6] and cumyl chloride (CumCl) were effective for IB polymerization in hydrocarbon media, in the presence of 2,6-di-*tert*-butyl-4-methylpyridine (DtBMP).[7] These experiments were conducted on a vacuum line where background moisture levels were ~1 ppm.[8] Despite these precautions, a 5−10-fold excess of DtBMP over diborane **1** with [**1**] = 2.0 mM was required to eliminate protic initiation in the absence of CumCl.

Polymerizations initiated by CumCl and **1** in the presence of DtBMP were characterized by low conversion (20−40%) and with initiator efficiencies (I_{eff}) ~ 100−300% consistent with ineffective chain transfer.[9] A reduction in [DtBMP] by a factor of 10 was accompanied by increases in conversion (up to 90%) and I_{eff} consistent with more effective chain transfer. These results suggested to us that facile termination of propagating chains, and/or decomposition of ion-pair **2** involving DtBMP[8] might be responsible (Scheme 1).

Scheme 1



Hindered pyridines such as DtBMP have long been recognized as "non-nucleophilic" bases.[10] Due to this property, they are valuable additives in living carbocationic polymerization.[11−13] A primary function is the removal of protic impurities, although the formation of common ions, resulting from reaction of pyridinium halides with excess Lewis acid, is now considered an important role in the context of living polymerization.[14]

In this communication, we demonstrate that DtBMP is not inert toward carbocations partnered with WCA. We also provide convincing evidence for the moderating effects of common ions on otherwise uncontrolled cationic polymerization processes.

As mentioned, direct reaction of ion-pair **2** (or the propagating chain) with DtBMP might account for decreased yields of PIB formed in its presence. To address this, the reactions of diborane **1** with CumCl in the presence of DtBMP in CD_2Cl_2 solution were studied by NMR spectroscopy.

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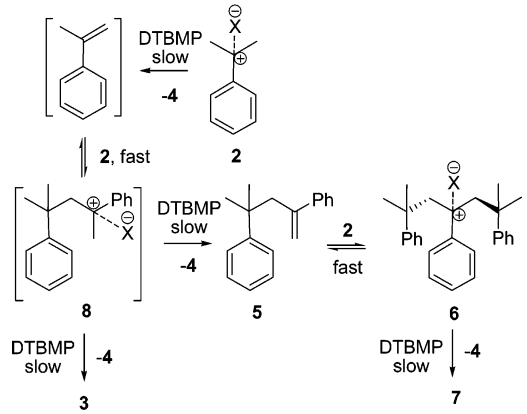
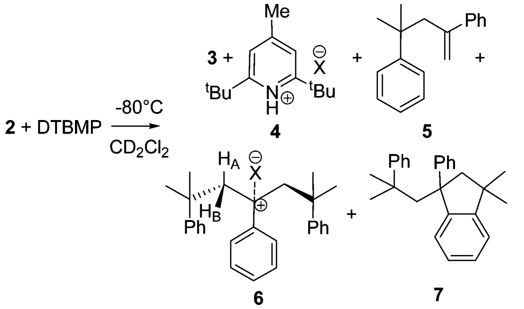
Scheme 2



In the absence of DtBMP, the ion-pair **2**, featuring the cumyl cation[15] partnered with the corresponding μ-Cl anion, is cleanly formed from CumCl and is stable in CD_2Cl_2 solution at low *T* (Scheme 1).[7] Decomposition of **2** is rapid only above −40 °C and the sole products are indan **3**,[16] HCl, and diborane **1**.

In the presence of DtBMP, the fate of ion-pair **2** is different (eq 1). Addition of excess DtBMP to a solution of ion-pair **2** (containing ~0.11 equiv of indan **3** and thus 0.22 equiv of HCl) in CD_2Cl_2 at −80 °C leads to instantaneous bleaching and formation of pyridinium salt **4** (1.21 equiv). There is some unreacted DtBMP (0.19 equiv), additional indan **3** is formed (corresponding to a total of 0.40 equiv of **2**), and the other identifiable products are olefin **5** (0.19 equiv of **2**) and the *stable* C_2-symmetric, carbocation **6** (0.12 equiv of **2**, $J_{AB} = 8.0$ Hz) as well as its corresponding cyclization product indan **7** (0.29 equiv of **2**).[17] These products correspond to >90% of the ion-pair **2** and indan **3** initially present.

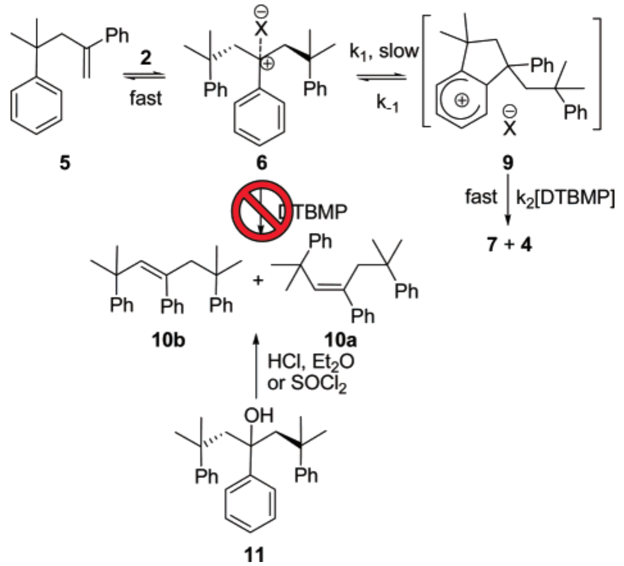


(1)

The formation of products analogous to **5** and **6** has been observed in the thermal decomposition of the *p*-methoxycumyl cation,[18] but this is the first time **6** has been detected in solution and certainly, the first time a 3° carbocation of this type has been detected in the presence of such a strong base!

Ion-pair **6** forms via (reversible) addition of ion-pair **2** to alkene **5 (**Scheme 2). Alkene **5** is formed via elimination from the corresponding ion-pair **8** [formed by the addition of ion-pair **2** to α-methylstyrene (α-Me−Sty)]. Since α-Me−Sty is unobserved, and ion-pair **2** is otherwise stable at this *T*, DtBMP is reacting directly with **2** (and **8**) to form the observed products as suggested in Scheme 2. However, any deprotonation involving DtBMP and **2** (or **8**) is slower than the various addition or cyclization reactions depicted—otherwise the major products would have been α-Me−Sty and alkene **5**. Note that regioselective formation of alkene **5** is expected if the base is sterically hindered; earlier work stressed the possible involvement of hindered pyridines in regioselective deprotonations of this type.[19,20]

Scheme 3



To address the reactivity of carbocation **6** toward DtBMP, we reacted preformed ion-pair **2** with alkene **5**. In the absence of DtBMP, consumption of **5** was instantaneous on mixing at −80 °C and a complex mixture of products was obtained; ion-pair **6** was not present though inter alia indans **3** and **7** or their degradation products formed.[15,18] However, when DtBMP was initially present in a mixture of diborane **1** and alkene **5** and ion-pair **2** was generated in situ through the addition of CumCl, much more reproducible and satisfactory results were obtained.

These solutions contained variable amounts of DtBMP and/or salt **4**, reflecting the stoichiometric control possible in NMR experiments on this scale (~0.01 M in diborane **1**). Interestingly, where all of the DtBMP added was in the form of salt **4**, it was possible to *observe* the addition of ion-pair **2** to alkene **5** to form **6** as this process was much slower at −80 °C. The rate of appearance of compound **6** exhibited second-order kinetics with a rate constant of 1.9 ± 0.2 M^{-1} s^{-1}or an initial addition rate constant $k_{in} = k[\mathbf{2}]_0$ of $\sim 3.6 \times 10^{-3}$ s^{-1} (see Supporting Information). The latter value is about 380× smaller than the pseudo-first-order rate constant (1.38 s^{-1}) determined for polymerization of α-Me−Sty using CumCl and excess $SnCl_4$ under similar conditions![21]

Though hindered alkene **5** will be less reactive toward addition than α-MeSty, it is surprising that the reaction of ion-pair **2**, which is either contact or solvent-separated in this solvent,[15] is so slow in the presence of excess common ion (~20 equiv). These results indicate that common ions do suppress “free” or at least reactive ion formation,[14] even for WCA in polar media.

Optimal conditions for the preparation of **6** involve the addition of a stock solution of CumCl to a mixture of diborane **1** and a 10-fold excess **5** in the presence of small quantities of DtBMP. Under these conditions formation of indan **3** is largely suppressed through quasi-irreversible formation of **6** in the presence of excess **5**. We could not completely eliminate formation of indan **7**, most likely due to the difficulty in maintaining the NMR tube at low *T* during mixing; this compound rapidly forms from **6** only at higher *T*.

On warming a solution of ion-pair **6** to −65 °C, the ion-pair decomposed completely over a period of about 30 min in the presence of 2−10 equiv of DtBMP to indan **7** and salt **4**. The kinetics were monitored at −65 °C at two different concentrations of DtBMP. The rate of disappearance of cation **6** was largely independent of [DtBMP] when the latter was increased by about a factor of 4 (see Supporting Information). There are two possible explanations for this behavior: (1) DtBMP is not directly involved in the formation of indan **7** even though salt **4** forms, or 2) DtBMP is not involved in the rate-determining step. With reference to Scheme 3 and eq 2, the latter scenario corresponds to a situation where the rate of reaction of an intermediate arenium ion **9** with DtBMP is fast compared to ring-opening to (reversibly) form **6**.

$$\frac{-\mathrm{d}[\mathbf{6}]}{\mathrm{d}t} = \frac{k_1 k_2 [\mathbf{6}][\mathrm{DTBMP}]}{k_{-1} + k_2[\mathrm{DTBMP}]}$$

$$\text{if } k_2[\mathrm{DTBMP}] \gg k_{-1} \; \frac{-\mathrm{d}[\mathbf{6}]}{\mathrm{d}t} \approx k_1[\mathbf{6}] \qquad (2)$$

The integral form of this rate equation is shown in eq 3. Regression analysis of the data provided estimates for $k_1 = 4.62 \times 10^{-5}$ s^{-1} and for $k_2/k_{-1} = 147$ M^{-1} (see Supporting Information). Cyclization of ion-pair **6** to form **9** is unfavorable and therefore $K = k_1/k_{-1} < 1$; that is, none of ion-pair **9** can be detected at low T in the absence of DtBMP. As a *conservative* estimate of the detection limits of ^{1}H NMR spectroscopy, we suggest that $K < 0.1$ or $k_{-1} > 4.62 \times 10^{-4}$ s^{-1} and therefore $k_2 > 6.8 \times 10^{-2}$ M^{-1} s^{-1}.

$$y = -\frac{k_1 k_2([\mathrm{DTBMP}]_o - [\mathbf{6}]_o)}{k_{-1}} t$$

$$y = \ln\left\{\frac{[\mathbf{6}][\mathrm{DTBMP}]_o}{[\mathbf{6}]_o[\mathrm{DTBMP}]}\right\} + A \ln\left\{\frac{[\mathbf{6}]}{[\mathbf{6}]_o}\right\} \qquad (3)$$

$$\text{with } A = \frac{k_2([\mathrm{DTBMP}]_o - [\mathbf{6}]_o)}{k_{-1}}$$

While reaction of DtBMP with **9** to form **7** is rapid, the rate would be ~28 × slower than the reaction of **2** with **5** at equivalent concentrations (vide supra). As the latter reaction can be considered a model for propagation in cationic polymerization, it is clear that the belief that DtBMP is inert toward propagating carbocations is only really true in a kinetic sense.

Surprisingly, competitve E$_1$-elimination to form alkenes **10a** and/or **10b**,[22] which might be expected in the presence of excess DtBMP, was not observed (Scheme 3). This is all the more surprising in view of our unsuccessful attempts to generate ion-pair **6** independently via ionization of the corresponding 3° chloride. Attempts to prepare this compound from the corresponding alcohol **11** under a variety of mild conditions invariably provided alkene **10a** and its isomer **10b** as the major products (see Supporting Information).

On the other hand, addition of HCl to a mixture of these alkenes, followed by diborane **1** at low T afforded varying amounts of ion-pair **6**, the cumyl cation **2**, indan **3** (formed from exo-alkene **5**), and indan **7** in accord with the reversibility implied in Schemes 2 and 3. The putative 3° chloride was not detected, even as an intermediate, in this reaction suggesting that the initial addition of HCl to these alkenes is unfavorable at −80 °C.

Thus, we suspect the failure of DtBMP to react directly with ion-pair **6** to form **10a** (or **10b**) is kinetic in origin. Molecular modeling shows that one side of the carbocation in contact ion-pair **6** is completely blocked by the counteranion (Figure 1a). In its most stable conformation, all of the α-protons are sterically shielded by either the counteranion or adjacent cumyl groups (Figure 1b). The lowest energy reactive conformation has one α-proton that is exposed, but this is partially blocked by one of the cumyl methyl groups (Figure 1c) such that abstraction by a hindered base should be kinetically slow.

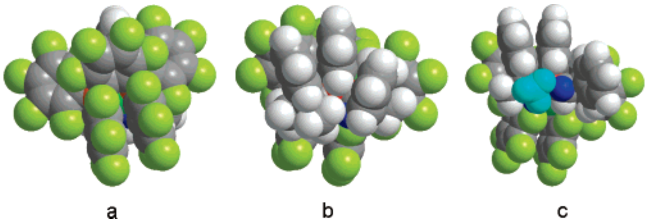


Figure 1. (a) Space-filling model of the most stable conformation (SE = −148.9 kcal mol^{-1}—this value is dominated by the attractive electrostatic interaction) of contact ion-pair **6** using the default MM2 force-field within Chem3D. The counteranion is depicted with F in light green, the bridging Cl anion in green (but is barely visible) and B in orange. (b) Space-filling model of the most stable conformation of contact ion-pair **6**. The cationic C atom is depicted in red while the α-protons are depicted in blue. (c) Space-filling model of the lowest energy reactive conformer (ΔSE = +2.0 kcal mol^{-1}) of ion-pair **6** with an α-proton anti-periplanar to the counteranion; this is partially blocked by one of the cumyl methyl groups depicted in cyan.

In conclusion, DtBMP *does react directly* with carbocations bearing α-protons though the particular reaction with **2** (or **8**), is significantly slower than propagation of α-Me−Sty. In a sufficiently hindered ion-pair such as **6**, cyclization occurs to the exclusion of elimination in the presence of DtBMP. Finally, our results stress the *profound* influence common ions have on moderating the reactivity of ion pairs partnered with WCA.

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Supporting Information Available: Text giving experimental procedures and figures showing the GC−MS analysis of DtBMP, representative mass spectra, kinetic data, and representative NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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(20) More recent work implicated sterically less hindered pyridines or related impurities, as being responsible for this type of chemistry in the case of 2,6-di-*tert*-butylpyridine and IB polymerization. (a) Bae, Y. C.; Faust, R. *Macromol. Symp.* **1998**, *132*, 11−23. (b) Bae, Y. C.; Faust, R. *Macromolecules* **1997**, *30*, 7341−7344. GC−MS analysis of commercially available DtBMP which had been sublimed failed to reveal the existence of sterically less-hindered, pyridine or imine bases (see Supporting Information).

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