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Electrophilic Reactivity of the α,α-Dimethylbenzyl (Cumyl) Cation

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ABSTRACT: The cumyl cation was generated by laser flash photolysis of cumyl tris(4-chlorophenyl)phosphonium tetrafluoroborate in CH_2Cl_2 and identified by its UV spectrum. From the decay of its absorbance at $\lambda = 335$ nm in the presence of variable concentrations of several nucleophiles with CC double bonds, rate constants for the reactions of the cumyl cation with these π-nucleophiles were determined. The linear free energy relationship $\log k_{20°C} = s(N + E)$ (eq 1) was used to calculate the electrophilicity parameter $E = 5.74$ of the cumyl cation from the rate constants determined in this work and the previously reported N and s parameters of the nucleophilic reaction partners. Substitution of E of the cumyl cation and of the previously reported N and s parameters of α-methylstyrene into eq 1 predicts the temperature-independent rate constant of the addition of the cumyl cation to α-methylstyrene (1.2×10^8 M^{-1} s^{-1}), which is relevant for the cationic polymerization of α-methylstyrene.

Introduction

Whereas there are numerous investigations about the rate of formation of the cumyl cation under solvolytic conditions[1] as well as about its heat of formation[2] and spectral identification under stable-ion conditions,[3,4] information about its electrophilic reactivity is rare.[5]

McClelland and Steenken generated the cumyl cation by laser-flash-induced photoprotonation of α-methylstyrene in 1,1,1,-3,3,3-hexafluoroisopropanol (HFIP) and measured the rates of its reactions with this solvent as well as with Br^- and alcohols in HFIP solution.[6,7] The failure to observe directly the cumyl cation by the same method in 2,2,2-trifluoroethanol (TFE) was explained by its estimated lifetime of < 20 ns, which is below the experimental limit of the instrumentation used.[7] Steenken reported that photoprotonation of bicumene in HFIP and subsequent fragmentation also yields the cumyl cation.[8] Second-order rate constants close to the diffusion limit were reported for the reactions of the cumyl cation with N_3^- or halide ions in HFIP.[8] Indirect evidence of the formation of the cumyl cation in TFE via a biphotonic pathway involving an intermediate bicumene radical cation has been obtained from the analysis of the resulting products.[8] Cozens generated the cumyl cation by irradiation of bicumene incorporated in a zeolite and measured the rate of its decay in zeolite cavities.[9]

The cumyl cation is of particular importance in macromolecular chemistry. On the one side, it is the active electrophile in Kennedy's INIFER process,[10,11] and on the other side, it is closely related to the propagating species in the carbocationic polymerization of α-methylstyrene.

To characterize the electrophilic reactivity of the cumyl cation, we have now measured the rates of the reactions of the cumyl cation with various π-systems in CH_2Cl_2 solution. These rate constants will then be used to calculate the electrophilicity parameter, E, of the cumyl cation according to eq 1

$$\log k_{20°C} = s(N + E) \qquad (1)$$

where E is an electrophilicity parameter, N is a nucleophilicity parameter, and s is a nucleophile-specific slope parameter, which is usually close to 1.[12,13]

A large body of data provides evidence that reactions of carbocations with CC double bonds follow eq 1.[13] The applicability of the linear free energy relationship approach (eq 1) for the prediction of propagation rate constants[14] has been demonstrated for the carbocationic polymerization of isobutylene,[15] *N*-vinylcarbazole,[16] styrene,[17] and 2,4,6-trimethylstyrene.[18]

In the accompanying paper, Dimitrov and Faust derived the propagation rate constant for the carbocationic polymerization of α-methylstyrene from competition experiments, where the dimer of the cumyl cation selected between different π-systems.[19] This article reports a fully independent approach to the same question, and from the agreement between the two methods, one can derive the reliability of the resulting rate constants.

Experimental Section

Materials. *Solvents.* For the laser flash photolysis experiments, p.a. grade dichloromethane (Merck) was subsequently treated with concentrated sulfuric acid, water, 10% $NaHCO_3$ solution, and again water. After predrying with anhydrous $CaCl_2$, it was freshly distilled over CaH_2. Acetonitrile (HPLC grade, VWR) and TFE (99%, Apollo) were used as received.

Precursors for Laser Flash Photolysis. α,α-Dimethylbenzyl chloride (97%, Apollo) was used as received. The phosphonium salts $Ph(CH_3)_2CPAr_3^+$ BF_4^- were prepared by reaction of α-methylstyrene with the corresponding triarylphosphonium tetrafluoroborate Ar_3PH^+ BF_4^-;[20] see the Supporting Information for details.

Nucleophiles. Allyltrimethylsilane (97%, Acros), 1-methylcyclopentene (98%, ABCR), (2,2-dimethyl-1-methylenepropoxy)trimethylsilane (98%, Aldrich), and *n*-butyl vinyl ether (98%, Aldrich) were used as received. Tetrabutylammonium bromide (99%, Aldrich) was dried under high vacuum for several hours and then handled in the glovebox.

Laser Flash Photolysis. Solutions of the cumyl derivatives ($A_{266\text{ nm}} \approx 0.9$, ca. 9×10^{-5} M) were irradiated with a 7 ns pulse from a quadrupled Nd/YAG laser (266 nm, 40−60 mJ/pulse), and a xenon lamp was used as a light source for UV/vis

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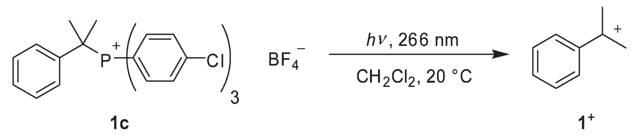
Scheme 1. Photolytic Generation of the Cumyl Cation



detection. The system is equipped with a fluorescence flow cell where the sample volume is replaced completely between subsequent laser pulses.

Kinetics were measured by following the decay of the cumyl cation at 335 nm. For each concentration, 64 or more individual decay curves were averaged, and the pseudo-first-order rate constants $k_{1\Psi}$ were obtained from the averaged curve by least-squares fitting to the single-exponential function $A_t = A_0 e^{-k_{1\Psi} t} + C$. The slope of a plot of $k_{1\Psi}$ versus concentration yields the second-order rate constant.

Spectra of **1**$^+$ were obtained as difference spectra from subsequent determinations without and with laser irradiation using an ICCD camera with a gate width of 10 ns and varying gate delay.

Results and Discussion

Laser-Flash-Photolytic Generation of the Cumyl Cation in Dichloromethane. Photolyses of carbon−halogen bonds have extensively been studied,[21,22] and Steenken reported that halide anions are excellent photoleaving groups for the laser-flash-photolytic generation of benzhydryl cations Ph_2CH^+ from various benzhydryl derivatives.[22a] However, photoheterolysis of neutral precursors requires polar solvents, such as acetonitrile or TFE,[23] whereas in nonpolar solvents such as CH_2Cl_2, only radicals are obtained.[22a] An alternative way to generate carbocations by photoheterolysis is the irradiation of phosphonium ions.[24] This method can also be employed in dichloromethane.[25]

When trying to generate the cumyl cation from cumyl chloride (**1a**) in acetonitrile or from cumyl triphenylphosphonium tetrafluoroborate (**1b**) in acetonitrile, TFE, or dichloromethane, we have not been able to obtain sufficient concentrations of the cumyl cation (in all cases $A_{\sim 330\text{nm}} < 0.04$).

In contrast, laser flash photolysis (266 nm, 40−60 mJ/pulse) of the cumyl tris(*p*-chlorophenyl)phosphonium tetrafluoroborate (**1c**) gave the cumyl cation (**1**$^+$) in dichloromethane solution in a concentration that is sufficient for measuring its reactivity (Scheme 1).

Identification. The transient spectrum (Figure 1, $\lambda_{max} \approx$ 335 nm) is very similar to the reported spectra of the cumyl cation in HFIP ($\lambda_{max} \approx 325$ nm)[6−8] and zeolite cavities ($\lambda_{max} \approx$ 330 nm).[9] Rapid mixing of α-methylstyrene and excess CF_3SO_3H in dichloroethane also yielded a spectrum with $\lambda_{max} \approx 336$ nm, which was attributed to the cumyl cation.[26] Furthermore, λ_{max} of 335 nm is in good agreement with the absorption maximum observed after treatment of cumyl chloride with SbF_5 in CH_2Cl_2 at −72 °C (λ_{max} = 333 nm; $\varepsilon_{333\text{ nm}} > 26\,300\ M^{-1}\ cm^{-1}$).[4] The absorption maxima in FSO_3H-SbF_5 (λ_{max} = 326 nm)[3b] and in 98% H_2SO_4 (λ_{max} = 324 nm)[3c] were found to be at slightly lower wavelengths. An analogous bathochromic shift of 5−15 nm was observed for benzhydrylium ions when going from solutions in acetonitrile or strong mineral acids to dichloromethane solution.[22a]

The lifetime of the 335 nm transient in CH_2Cl_2 is ~0.2 μs. Its cationic nature is in line with the fact that it was not observable when the photolysis was carried out in the presence of 1.0×10^{-3} M tetrabutylammonium bromide. Under these conditions, the collapse of the resulting cumyl cation−bromide ion pair proceeds so fast that the carbocation cannot be detected with the instrumentation used (limit ≈ 10−20 ns).

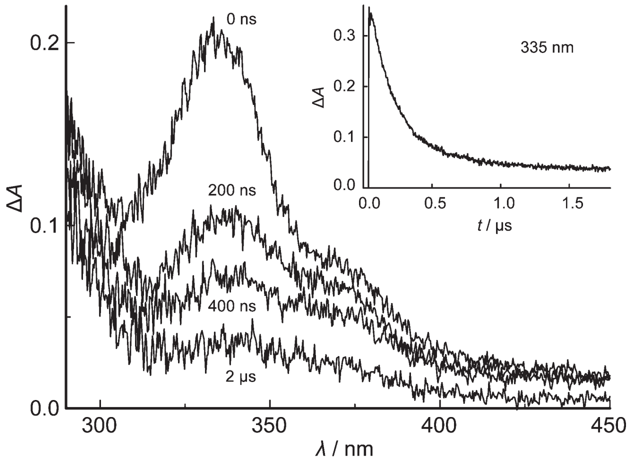


Figure 1. Transient spectra obtained 0 ns, 200 ns, 400 ns, and 2 μs after 266 nm irradiation of cumyl tris(4-chlorophenyl)phosphonium tetrafluororoborate (8.9×10^{-5} M, $A_{266\text{nm}}$ = 0.9) in CH_2Cl_2. The inset shows the decay at 335 nm during the first 1.8 μs.

The fast decay of the transient with λ_{max} = 335 nm is superimposed by a slower decay ($1/k \approx 7$ to 8 μs) of a broad absorption band in the range of 330−380 nm. The rate of decay of this species (measured at 335 nm) is not affected by bromide, which suggests a radical species. Steenken reported that the spectrum of the cumyl radical obtained by pulse radiolysis in CH_2Cl_2 shows λ_{max} at 265 nm and two smaller absorption maxima at 308 and 320 nm.[8] Furthermore, $Ph_3P^{\bullet +}$ and $(p\text{-Cl-}C_6H_4)_3P^{\bullet +}$ have been reported to absorb in this range.[27] Therefore, the formation of cumyl radicals and phosphinium radical cations by homolytic photocleavage of the precursor are considered to be a plausible explanation for the residual absorption.

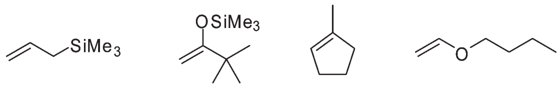
We had problems observing the cumyl cation in TFE or in acetonitrile, which is rationalized by the higher nucleophilicity and basicity of these solvents compared with CH_2Cl_2; the appearance of a weak absorbance at ~330 nm in TFE will be discussed below.

Influence of the Photoleaving Group. It is interesting that the cumyl cation is much more efficiently generated from the precursor with the $(p\text{-Cl-}C_6H_4)_3P$ than with the Ph_3P photoleaving group. Because both phosphines can be expected to undergo diffusion-controlled reactions with carbocations of high electrophilicity ($E > 3$),[28] one can conclude that the difference in the efficiency of carbocation formation from $PhC(CH_3)_2{-}PPh_3^+\ BF_4^-$ (**1b**) and $PhC(CH_3)_2{-}P(p\text{-Cl-}C_6H_4)_3^+\ BF_4^-$ (**1c**) is not due to external return of Ar_3P but results from different behavior within the geminate solvent cage. $(p\text{-Cl-}C_6H_4)_3P$ is less nucleophilic than Ph_3P ($\Delta N = 1.75$),[28] less basic ($\Delta pK_{AH} = 1.7$ in H_2O),[29] and less easily oxidized ($\Delta E^0_{ox} = 0.22$ V in CH_3CN).[30]

If one assumes that the photolytic generation of the carbocation proceeds via initial homolytic cleavage and subsequent electron transfer,[21,23,24b] then the higher yield of **1**$^+$ from **1c** might be rationalized by the higher reduction potential of $(p\text{-Cl-}C_6H_4)_3P^{\bullet +}$. This explanation is unlikely, however, because the benzhydryl cation Ph_2CH^+ can readily be generated from $Ph_2CH{-}PPh_3^+\ BF_4^-$ though the oxidation potential of $Ph_2CH^\bullet$ is even higher than that of the cumyl radical.[31]

Because carbocations can only be observed on this time scale if they escape from the geminate solvent cage faster than they recombine with the photoleaving group, the

Scheme 2. π-Nucleophiles



2a **2b** **2c** **2d**

different nucleophilicity of the phosphines may account for the increased efficiency with the (p-Cl-C_6H_4)$_3$P leaving group. However, as stated above, the parent benzhydryl cation can be generated from $Ph_2CH{-}PPh_3^+\ BF_4^-$, although its electrophilicity is comparable to that of the cumyl cation. (See below.)

We therefore assume that it is the higher Brønsted basicity of triphenylphosphine compared with (p-Cl-C_6H_4)$_3$P that rapidly deprotonates the cumyl cation and thus is responsible for the failure to generate the cumyl cation by photoheterolysis of $PhC(CH_3)_2{-}PPh_3^+\ BF_4^-$ (**1b**).

This interpretation is in agreement with observations by Thibblin, who investigated the solvolyses of cumyl derivatives in 25% (v/v) aqueous acetonitrile, which proceed via intermediate cumyl cations.[5d] Because the ratio α-methylstyrene/cumyl alcohol increases with the basicity of the leaving group, it was concluded that a significant amount of the elimination product is generated in the initial ion pair.

Rates of the Reactions of Cumyl Cations with π-Systems. When the laser flash photolysis of **1c** (Scheme 1) was carried out in the presence of a high excess of the π-nucleophiles **2a**–**d** (Scheme 2), exponential decays of the cumyl cations' absorbance at 335 nm were observed, from which the pseudo-first-order rate constants $k_{1\Psi}$ were obtained. Plots of $k_{1\Psi}$ against the concentrations of the nucleophiles were linear, as shown for a typical example in Figure 2.

The large intercepts of these plots ((5–8) × $10^6\ s^{-1}$) reflect the fast decay of the cumyl cation in CH_2Cl_2 solution. The magnitude of the intercept varied somewhat between different experiments, reflecting variable concentrations of water and other impurities in different batches of dichloromethane. The slopes of these plots represent the second-order rate constants k_{obs} that are reported in Table 1.

Only nucleophiles within a narrow range of reactivity could be employed to characterize the electrophilic reactivity of the cumyl cation: Because of the fast decay, the rate constant had to be greater than $\sim 10^7\ M^{-1}\ s^{-1}$, but it had to be less than $\sim 2 \times 10^8\ M^{-1}\ s^{-1}$ not to approach the limit of diffusion control where eq 1 cannot be employed.

Allyltrimethylsilane (**2a**) is the least reactive nucleophile for which a reliable rate constant could be determined: Even at the highest concentration used ([**2a**] = 0.25 M), only one-third of the measured pseudo-first-order rate constant $k_{1\Psi}$ is due to the reaction with allyltrimethylsilane, whereas two-thirds correspond to the background reaction. For less reactive nucleophiles, the slope of the $k_{1\Psi}$ versus [**2**] plot is so small that a large error of the second-order rate constant will result.

According to eq 1, the electrophilicity parameter $E = 5.74$ for the cumyl cation (**1**$^+$) is obtained from a plot of (log k_{obs})/s versus the nucleophilicity parameter N of **2a**–**c** (Figure 3). As expected from the good correlation in Figure 3, Table 1 shows that the calculated rate constants for **1**$^+$ + **2a**, **2b**, and **2c** agree well with experimental values. The calculated value for the reaction of **1**$^+$ with ethyl vinyl ether is 4 times larger than that measured for the reaction of **1**$^+$ with n-butyl vinyl ether (Table 1).

The similarity of the E parameters of the cumyl cation **1**$^+$ ($E = 5.74$) and the benzhydryl cation Ph_2CH^+ ($E = 5.90$)[13] is another example for the rule-of-thumb that one phenyl group has a similar stabilizing effect on carbocations as two methyl groups.[32]

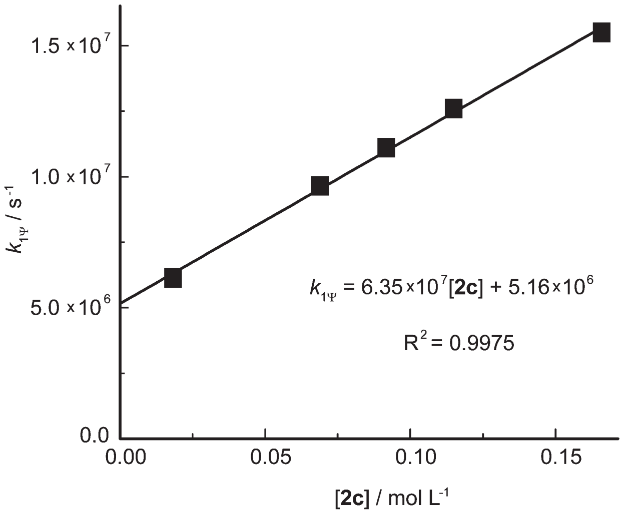
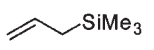
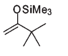
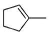
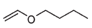
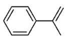


Figure 2. Plot of the pseudo-first-order rate constants $k_{1\Psi}$ obtained from reaction of the cumyl cation **1**$^+$ with 1-methylcyclopentene (**2c**) in CH_2Cl_2 against the concentration of **2c**.

Table 1. Experimental Rate Constants ($M^{-1}\ s^{-1}$) for the Reactions of **1**$^+$ with π-Nucleophiles 2a–d in CH_2Cl_2 (Laser Flash Photolysis, 20 °C) and Comparison with Values Calculated from Equation 1

nucleophile	N (s)[a]	k_{obs} / $M^{-1}\ s^{-1}$	k_{calc}[b] / $M^{-1}\ s^{-1}$
2a 	1.79 (0.94)	1.22 × 10^7	1.20 × 10^7
2b 	3.78 (0.79)	3.46 × 10^7	3.32 × 10^7
2c 	1.37 (1.10)	6.35 × 10^7	6.62 × 10^7
2d 	3.92 (0.90)[c]	1.18 × 10^8	4.94 × 10^8 [c]
2e 	2.35 (1.00)	–[d]	1.23 × 10^8

[a] From ref 13. [b] From eq 1 using $E = 5.74$. [c] N, s parameters and k_{calc} for ethyl vinyl ether. [d] Not determined because the nucleophile absorbs at the wavelength of the excitation.

Parr's global electrophilicity index, ω,[33] which has previously been determined for the cumyl (12.8) and the benzhydryl cation (13.0),[34] also predicts similar electrophilic reactivities of these two carbenium ions. From ω_C, the local electrophilicity at the carbocation site,[34a] one would predict that the cumyl cation ($\omega_C = 5.57$) is considerably more electrophilic than the benzhydryl cation Ph_2CH^+ (ω_C = 4.61),[34] in contrast with our observations.

Comparison with Other Kinetic and Thermodynamic Data. *Reactions with Solvents.* Equation 1 can also be employed for reactions of carbocations with solvents; first-order rate constants k_1 are obtained when the solvent-specific parameters N_1 and s are substituted in eq 1.[35] As shown in Table 2, a first-order rate constant of 2.5 × $10^6\ s^{-1}$ is calculated for the reaction of the cumyl cation (**1**$^+$) with the solvent trifluoroethanol.

Previous investigations[7,8] indicated a fast decay of the cumyl cation in TFE solution, and a decay rate constant > 5 × $10^7\ s^{-1}$ has been suggested.[7] In our experiments, laser flash photolysis of **1c** in TFE gave rise to a small absorbance at $\lambda \approx$ 330 nm, but because of the low absorbance ($A < 0.04$), it was not possible to obtain a spectrum or measure its decay rate reliably. A rough estimate for the decay of this absorbance gives a rate constant (5 × $10^6\ s^{-1}$) close to the calculated value.

Using the azide clock method, Thibblin determined a first-order rate constant of $\sim 5 \times 10^9\ s^{-1}$ for the reaction of the

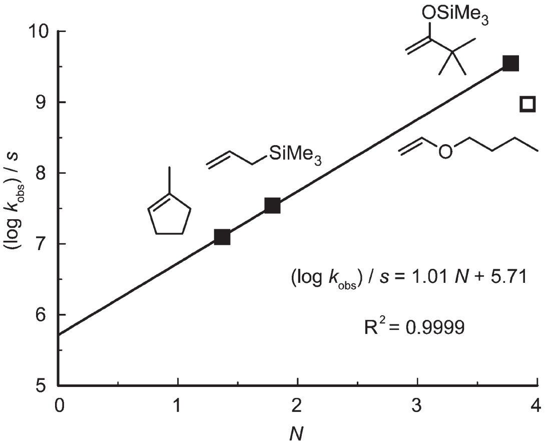


Figure 3. Plot of (log k_{obs})/s versus N for the reactions of the cumyl cation ($\mathbf{1}^+$) with the π-systems **2a**−**c** (■). When the slope is set to unity as required by eq 1, one obtains $E = 5.74$. For *n*-butyl vinyl ether (□), the N, s parameters are not known, and those of ethyl vinyl ether were used. This value was not used for the correlation.

Table 2. First-Order Rate Constants (s^{-1}) for the Reaction of the Cumyl Cation (1^+) with Solvents and Comparison with Values Calculated from Equation 1

solvent[a]	N_1 (s)[b]	k_1/s^{-1}	$k_{1,calc}/s^{-1}$[c]
TFE	1.23 (0.92)	($> 5 \times 10^7$)[d]	2.5×10^6
25AN75W	5.04 (0.89)[e]	$\sim 5 \times 10^9$[f]	3.9×10^9
50T50W	3.57 (0.89)	1.7×10^{10}[g]	1.9×10^8

[a] Mixtures of solvents are given as (v/v). AN: acetonitrile, T: TFE, W: water. [b] From ref 35. [c] Calculated from eq 1. [d] Laser flash photoprotonation of α-methylstyrene;[7,8] lower limit derived from the fact that the lifetime was less than the experimental limit of 20 ns. [e] Interpolated; solvent nucleophilicity parameters are virtually constant for solvent mixtures 20AN80W to 50AN50W.[35] [f] By azide clock method.[5d] [g] By azide clock method.[5a,b]

cumyl cation ($\mathbf{1}^+$) with 25AN75W[5d] close to the calculated value of 3.9×10^9 s^{-1} (Table 2). Because of the lower nucleophilicity of 50T50W,[35] we would expect a considerably slower decay of the cumyl cation ($\mathbf{1}^+$) in this solvent ($k_{1,calc} = 1.9 \times 10^8$ s^{-1}), and we cannot explain why the azide clock method gave a higher decay rate constant for the cumyl cation in 50T50W ($k_1 = 1.7 \times 10^{10}$ s^{-1})[5a,b] than in 25AN75W.

Comparison with Solvolysis Rates. Solvolysis rate constants, k_s, of cumyl chloride have been measured by Brown[1a] and Liu[1b] in different solvents. From the reported k_s values, an estimate for the electrofugality of the cumyl cation $E_f \approx -4.99$ has been derived,[36b] indicating that cumyl derivatives solvolyze ~10 times faster than the corresponding benzhydryl derivatives (for Ph_2CH^+, $E_f = -6.05$).[36] The difference in the solvolysis rates of $PhC(CH_3)_2Cl$ and Ph_2CHCl in various solvents is not reflected by the almost equal electrophilicities of the resulting carbenium ions.

Comparison with Thermodynamic Parameters. Arnett and Hofelich have established a carbenium ion stability scale based on the heats of reaction, ΔH_{rxn}, of alcohols with $HSO_3F/SbF_5/SO_2ClF$ at −55 °C (eq 2).[2b]

$$\mathrm{ROH} \xrightarrow[\Delta H_{rxn}]{HSO_3F/SbF_5/SO_2ClF} R^+ \qquad (2)$$

By this method, the cumyl cation ($\Delta H_{rxn} = -168.7$ kJ mol^{-1}) turns out to be slightly more stabilized than the parent benzhydryl cation ($\Delta H_{rxn} = -164.5$ kJ mol^{-1}), in line with the relative solvolysis rate constants.

Only crude estimates of the pK_R value for the reaction of water with the cumyl cation are available (−10.1 to −12.3),[5b,31a] and we refrain from comparing it with that of the benzhydryl cation.

Rate Constant for the Addition of the Cumyl Cation to α-Methylstyrene. A direct kinetic determination of the first step of the carbocationic polymerization of α-methylstyrene, that is, the reaction of the cumyl cation ($\mathbf{1}^+$) with α-methylstyrene (**2e**) to form the dimeric cation, was not attempted because α-methylstyrene absorbs at the excitation wavelength of the laser and interferes with the photolytic generation of the cumyl cation. Furthermore, the UV-absorption spectra of the cumyl ($\lambda_{max} = 335$ nm) and the dimeric cation ($\lambda_{max} = 348$ nm)[37] are very similar, which complicates measuring the rate of consumption or formation of the carbocations.

Using the known nucleophilicity parameter of α-methylstyrene ($N = 2.35$, $s = 1.00$)[13] and the E value of 5.74 for the cumyl cation determined in this work, eq 1 yields $k_{calc,20°C} = 1.2 \times 10^8$ M^{-1} s^{-1} for the rate of the reaction of the cumyl cation with α-methylstyrene. Because bimolecular reactions of such high rates do not have enthalpic barriers,[14a,38] this rate constant can be considered to be almost independent of temperature.

The rate constant calculated in this way is 400 times higher than the value reported previously by the Paris laboratory for the addition of the cumyl cation to α-methylstyrene at −65 °C, which was obtained from the initial slopes of appearance of a 348 nm absorbance band ascribed to the dimeric cation.[37]

Although previous investigations on styrene derivatives showed similar electrophilic reactivities of monomeric and dimeric cations,[17,18] we cannot generalize this observation. Because we were not able to synthesize suitable precursors for the laser flash photolytic generation of the dimeric cation, we leave the investigation of the oligomeric cations to the following paper.[19]

Acknowledgment. Dedicated to Professor Oskar Nuyken on the occasion of his 70th birthday. We thank Professor R. Faust for stimulating this investigation and the Deutsche Forschungsgemeinschaft for financial support.

Supporting Information Available: Syntheses and characterization of the phosphonium salt precursors and detailed kinetic data for the reactions of the cumyl cation with π-nucleophiles. This material is available free of charge via the Internet at http://pubs.acs.org.

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