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Reactivity of Benzyl Cation and of Benzhydryl Cation with Alkenes in Solution: Initiation Step in Cationic Polymerization[1]

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ABSTRACT: The pulse radiolysis technique has been used to determine rate constants for the initiation step in cationic polymerization. The reactivity of the benzyl cation and of the benzhydryl cation toward some 13 alkenes in dichloroethane solution has been determined. The rate constants vary over four orders of magnitude with the molecular structure of the nucleophiles. The reactivity–molecular structure dependence is discussed.

Pulse radiolysis studies of the reactivity of phenylcarbenium ions in solution[2-5] have provided new information about a class of reaction of importance in the field of polymer chemistry. We refer to the process of cationic polymerization[6-10] and specifically to the initiation step of this process. We have generated the benzyl cation and the benzhydryl cation on a submicrosecond time scale[5] in 1,2-dichloroethane solution and have determined rate constants for reactions of these ions with some 13 different alkenes. These phenylcarbenium ions, generated by an electron pulse,[2,11] are free of complexities such as ion pairing and cation aggregation which may be encountered when cationic polymerization is induced chemically, as with strong acid,[12-14] with iodine,[15] with Friedel–Crafts reagents,[16,17] or with carbocation salts.[18,19] The reaction observed here is the single-step condensation reaction of cation with alkene exclusive of any propagation reaction. The reactivity–molecular structure relationship is of interest not only from the point of view of polymer chemistry, but also with respect to carbenium ion reactivity, for the alkenes are a class of nucleophile for which carbocation reactivity has not, heretofore, been determined directly.

Experimental Section

As previously described,[20,21] the source of the electron pulse was a Varian V-7715A electron linear accelerator, delivering 3–4 MeV electrons at a pulse current of about 300 mA for pulses of 100–400 ns duration and about 600 mA for pulses of 80 ns duration or less. The 80 ns pulses were used in most of the following experiments. The concentration of transients produced was on the order of 10^{-6} M or lower. All of the runs were done at 24 ± 1 °C. The transient absorptions were observed with either an RCA 1P28 or RCA 7200 photomultiplier as the detector. A Bausch and Lomb grating monochromator, type 33-86-25, f/3.4, was used.

Our standard 20-mm reaction cells with high purity silica windows were used in all experiments with, generally, a double pass of the analyzing light beam. A detailed description of the optical arrangement and the detection system has been presented.[20,21]

Table I
Rate Constants for the Reactions of the Benzyl Cation and of the Benzhydryl Cation with Alkenes in 1,2-DCE at 24 °C[a]

alkene	$PhCH_2^+$	Ph_2CH^+
ethylene	$<10^5$	
propylene	1.9×10^6	$<10^5$
isobutylene	1.9×10^7	9.5×10^6
3,3-dimethyl-1-butene	2.2×10^6	
allyl benzene	1.5×10^6	
cyclohexene	9.4×10^6	
1,3-cyclohexadiene	2.7×10^7	1.5×10^7
1-phenylcyclohexene		7.4×10^7
1,3-butadiene	8.7×10^5	$<10^5$
2-methyl-1,3-butadiene		7.1×10^6
2,3-dimethyl-1,3-butadiene		2.7×10^7
4-methyl-1,3-pentadiene		2.5×10^8
2,4-dimethyl-1,3-pentadiene		1.0×10^9

[a] Units are M^{-1} s^{-1}. All of the rate constants, save two, have an experimental uncertainty of ±15%. The uncertainty is ±25% for the rate constants for the benzyl cation with 1,3-butadiene and for the benzhydryl cation with 1,3-cyclohexadiene.

1,2-Dichlorethane (DCE) was 99+% gold label obtained from Aldrich Chemical. Dibenzylmercury was obtained from Alfa Inorganics; diphenylmethyl bromide, technical grade, was from Chemical Samples Co. The method of purification of these compounds has been described.[2,4] Anhydrous ammonia, 99.99% purity, ethylene, c.p. grade, 99.5% purity, propylene, c.p. grade, 99.5% purity, and 1,3-butadiene, instrument purity, 99.5% minimum purity, were all obtained from Matheson and used without further purification. Research grade isobutylene, 99.93% purity, was obtained from Phillips Petroleum Co. and was also used as obtained. The foregoing compounds were all stored under vacuum in the dark.

The following compounds, all obtained from Aldrich Chemical, were subjected to vacuum distillation and stored under vacuum and refrigerated: 3,3-dimethyl-1-butene (neohexene) 99%, cyclohexene 99%, 1,3-cyclohexadiene 99%, 2-methyl-1,3-butadiene (isoprene, MBD) 99+% gold label, 2,3-dimethyl-1,3-butadiene (DMPD) 98%, 4-methyl-1,3-pentadiene (MPD) 98%, and 2,4-dimethyl-1,3-pentadiene (DMPD) 98%. Allylbenzene and 1-phenylcyclohexene, 99%, from Aldrich, were purified by partial freezing.

In order to obtain the concentration of the gaseous alkenes in 1,2-DCE, the solubilities of ethylene, isobutylene, and 1,3-butadiene in DCE were measured. The results are ethylene, 0.95 mol % at 927.8 torr, isobutylene, 1.07 mol % at 131 torr, and 1,3-butadiene, 1.08 mol % at 90.2 torr. For the experiments with

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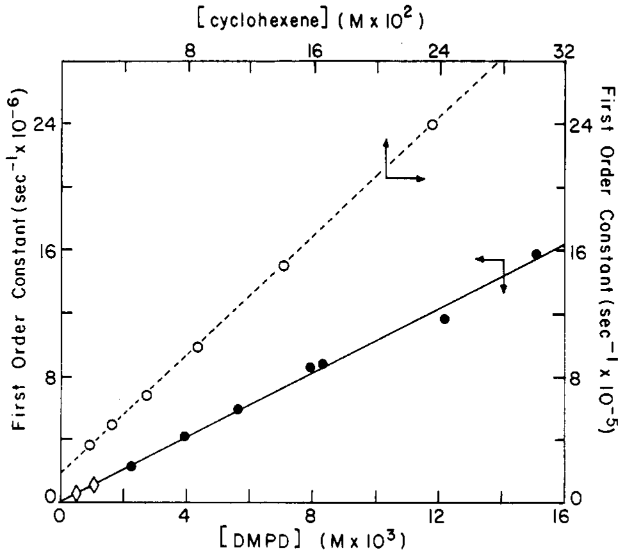


Figure 1. Plot of the pseudo-first-order rate constant vs. concentration of the nucleophile for the reactions of phenylcarbenium ions with the nucleophile in 1,2-DCE at 24 °C: (○) benzyl cation (monitored at 364 nm) with cyclohexene; (●) benzhydryl cation (monitored at 449 nm) with DMPD; (◇) obtained by monitoring the formation of the tetrasubstituted allyl cation at 312 nm.

isobutylene, 1,3-butadiene, and propylene, at least 90% of the volume of the reaction cell system was occupied by DCE. For the experiments with ethylene, at least 98% of the reaction cell volume was occupied by DCE. Under these conditions, and assuming Henry's law holds, at least 99% of the alkene gases in the reaction cell volume were dissolved in the DCE.

Results and Discussion

Rate constants have been determined in 1,2-DCE solution at 24 °C for reaction of the benzyl cation and of the benzyhydryl cation with the various unsaturated compounds. The values obtained are all shown in Table I. The benzyl cation was formed from dibenzylmercury in solution and the benzhydryl cation from benzhydryl bromide in solution[2,5] during an 80 ns electron pulse. The benzyl cation was monitored at 364 nm and the benzhydryl cation at 449 nm, at or near the maxima of their optical absorption bands.[2,3,5] The benzhydryl cation is the sole transient absorber at 449 nm. In the case of the benzyl cation, there is a weak overlapping absorption at 364 nm from another transient which exhibits a maximum at 323 nm. This latter species has a reaction lifetime which is at least an order of magnitude longer than the reaction lifetime of the benzyl cation with the nucleophile present, so that a well-defined plateau in the decay curve of the cation is obtained.

The reaction of the phenylcarbenium ion was carried out at a sufficiently high concentration of the nucleophile so that the reaction was pseudo-first-order and fast enough to compete overwhelmingly with the natural decay of the cation by combination with Cl⁻:

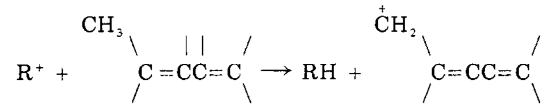
$$PhCH_2^+ + Cl^- \rightarrow PhCH_2Cl \quad (1)$$

$$PhCH_2^+ + CH_3CH{=}CH_2 \rightarrow CH_3\overset{+}{C}HCH_2CH_2Ph \quad (2)$$

The individual rate curves, in all cases, were found to fit a first-order rate law. The values of these constants, such as k_2, were then determined by plotting the first-order constants against the concentration of the alkene, generally over a five- to tenfold concentration range. From the slopes of the straight lines, such as those shown in Figure 1 for cyclohexene and for 2,4-dimethyl-1,3-pentadiene, the rate constants shown in Table I were obtained. The values of the rate constants are all below the diffusion controlled limit and range over four orders of magnitude; the effect of molecular structure on the reactivity is thus fairly large in these systems.

The reaction of these arylcarbenium ions with the alkenes most likely proceeds by the condensation reaction, as shown in (2), although two other possibilities merit consideration. These are electron transfer and hydride transfer (where there is a methyl substitute at the double bond). The electron transfer is ruled out since the ionization potentials of the benzyl radical and the benzhydryl radical, 7.76 and 7.32 V, respectively, are lower than the ionization potentials[22] of the alkenes used: ethylene 10.5 V, propylene 9.73 V, isobutylene 9.35 V, 1,3-butadiene 9.24 V, and 2,3-dimethyl-1,3-butadiene 8.72 V. The product of electron transfer would be a radical cation of the alkane, a type of species whose spectrum has been observed[23] in low-temperature glasses. No such radical cations have been observed in our experiments.

Hydride transfer would yield a stable, neutral molecule and an allylic carbenium ion when the alkene contains two conjugated double bonds. Thus, the hydride transfer reaction with the methyl-substituted 1,3-butadiene would yield a dienyl cation:

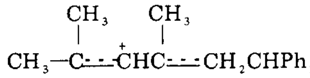


$$R^+ + (CH_3)C{=}C(-)(-)C{=}C \longrightarrow RH + (\overset{+}{C}H_2)C{=}CC{=}C \quad (3)$$

which has an absorption band at about 400 nm.[24] No such dienyl cation was observed with various substitued 1,3-butadienes. Similarly, no measureable rate ($k_4 < 10^5$) could be seen for the reaction:

$$PhCH_2^+ + Ph_3CH \rightarrow PhCH_3 + Ph_3C^+ \quad (4)$$

with the concentration of triphenylmethane as high as 0.15 M. A direct indication of the occurrence of the condensation reaction is seen in the reaction of the benzhydryl cation with 2,4-dimethyl-1,3-pentadiene, the product of which is a tetrasubstituted allylcarbenium ion,



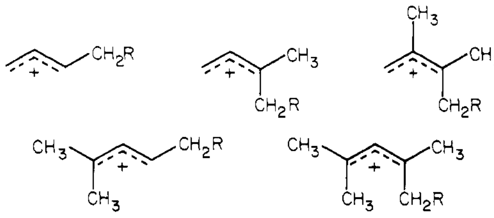
$$CH_3{-}\underset{}{\overset{CH_3}{\overset{|}{C}}}{\cdots}\overset{+}{C}H\overset{CH_3}{\overset{|}{C}}{\cdots}CH_2CHPh_2$$

The optical absorption spectrum of this species is known; it has a UV band at 305 nm.[24,25] Pulse radiolysis of a solution of benzhydryl bromide and DMPD yields a complex spectrum (three species) which may be deconvoluted to reveal an absorption band at 312 nm which is not affected by oxygen. We believe this is the allyl carbenium ion.

The relationship between reactivity and molecular structure is best seen by discussing the nucleophiles in separate groups. The rate constants in the series ethylene ($<10^5$) < propylene (1.9×10^6) < cyclohexene (9.4×10^6) < isobutylene (1.9×10^7), for which the values extend over two orders of magnitude, increase by almost an order of magnitude at each step. The rate constants correlate with the nature of the carbenium ion product formed in the reaction. Thus, with ethylene, a primary carbenium ion is formed. With propylene and cyclohexene a secondary ion is formed, and with isobutylene a tertiary ion is formed. The rate constants thus increase with increasing stability of the product ion, the tertiary ion being the most stable. It is well known in polymer chemistry that isobutylene undergoes cationic polymerization quite readily whereas ethylene does not.

This correlation of the rate constants with the stability of the product ion suggests that a linear free energy relationship should hold for the reactions of the foregoing nucleophiles. Thus, if the entropy change is small for such reactions (as is usually the case) and the Arrhenius preexponential factor is the same for each reaction, a single linear relationship between log *k* and the heat of reaction, ΔH, should hold. By estimating values of ΔH from appropriate gas phase ionization potentials and gas phase bond energies, the plot of log *k* vs. ΔH (over the range -5 to -18 kcal/mol) is found to be linear. However, the magnitude of the uncertainty in the value of ΔH for these reactions is sufficiently large that it does not seem worthwhile to present the details here.

The effect of methyl substitution on the reactivity of several 1,3-conjugated dienes toward the cation is readily seen in the sequence of reactions with benzhydryl cation: BD ($<10^5$) < MBD (7.1×10^6) < DMBD (2.7×10^7) < MPD (2.5×10^8) < DMPD (1.0×10^9). The nature of the product ion formed in each case, in the same order (where R represents Ph_2CH), is:



The rate constant again correlates with the stability of the product ion which is strongly affected by methyl substitution.

We may examine the sequence allylbenzene (1.5×10^6), propylene (1.9×10^6), and neohexene (2.2×10^6) reacting with the benzyl cation to see whether the effect of substituents is in the normal inductive order, namely $(CH_3)_3C > CH_3$. We must conclude, in view of the experimental uncertainty, ±15%, that the foregoing sequence does not demonstrate a trend, the rate constants for propylene and neohexene being essentially the same.

Lastly, we take note of the sequence BD (8.7×10^5), propylene (1.9×10^6), cyclohexene (9.4×10^6), and cyclohexadiene (2.7×10^7). Here the observation that BD (which yields an allyl cation) is less reactive than propylene (which yields a secondary cation) calls for some explanation, since the relative reactivity seems inconsistent with the correlation of product ion stability. Cyclohexadiene, it will be noted, is more ractive than cyclohexene. The lesser reactivity of BD, compared with propylene, may very well be an illustration of an empiricism which is referred to as the principle of least motion, which was suggested some time ago by Rice and Teller[26] and which has been discussed recently by Hine.[27] The suggestion of Rice and Teller was that "those elementary reactions will be favored that involve the least change in atomic position and electronic configuration". This empiricism may be considered in two parts, of which the first is the principle of least nuclear motion. Change in nuclear position in the reaction results from changes in bond length and in bond angle. It has been suggested[27] that the sum of the squares of the changes in bond orders (approximately proportional to the sum of the squares of bond lengths) is a crude measure of the extent of nuclear motion resulting from changes in bond lengths.

Formation of the allylic cation is accompanied by shortening of the carbon–carbon single bond and lengthening of the carbon–carbon double bond. The sum of the squares of the changes in bond order in this reaction[28] is 1.5. In the reaction with propylene, the product of which is a secondary cation, the magnitude of this quantity[28] is 1.0. This difference of 0.5 in the squares of the changes in bond order correlates with the higher reactivity of propylene and may be considered, by some, to be consistent with the principle of least nuclear motion. Similar correlations have been reported[26] for some H-atom abstraction reactions.

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References and Notes

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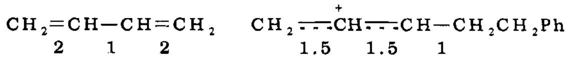
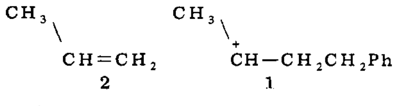
(28) In the case of BD, the reactant and product have bond orders as shown



$$\mathrm{CH_2\underset{2}{=}CH\underset{1}{-}CH\underset{2}{=}CH_2} \qquad \mathrm{CH_2\underset{1.5}{\cdots}\overset{+}{C}H\underset{1.5}{\cdots}CH\underset{1}{-}CH_2CH_2Ph}$$

giving $(2-1.5)^2 + (1-1.5)^2 + (2-1)^2 = 1.5$. In the case of propylene we have



$$\mathrm{CH_3{-}CH\underset{2}{=}CH_2} \qquad \mathrm{CH_3{-}\overset{+}{C}H\underset{1}{-}CH_2CH_2Ph}$$

giving $(2-1)^2 = 1.0$.