Reactions of Substituted Vinyl Cations in Acetonitrile Solution as Studied by Flash Photolysis

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Vinyl cations $\text{I}^+$ of the structure $\text{R}^1\text{C}^+\text{C}^=\text{CR}^2$ ($\text{I}^+$: $\text{R}^1 = \text{R}^2 = \text{anisyl}; \text{I}^*\text{: R}^1 = \text{phenyl}, \text{R}^2 = \text{anisyl}; \text{I}^*\text{: R}^1 = \text{methyl}, \text{R}^2 = \text{anisyl}$) were generated by flash photolysis of corresponding bromides. Lifetime measurements yielded the following: substitution of aromatic groups in 2-position by methyl groups largely improved the electrophilicity of the vinyl cations. The nucleophilicity of typical compounds (ketone, ester, alcohol, olefin) was measured.

Introduction

The reactivity of carbocations is still a subject attracting the interest of researchers investigating the fundamentals of nucleophilicity and especially problems concerning the interdependence of reactivity and selectivity [1–5]. This paper deals with reactions of substituted vinyl cations of the structure $\text{I}^+$

$$\begin{align*}
\text{R}^1&\text{C}=\text{C}^+\text{R}^2 \\
\text{I}^+&
\end{align*}$$

and concerns two aspects: (i) the nucleophilicity of various compounds toward vinyl cations ($\text{I}^+$) and (ii) the electrophilicity of vinyl cations ($\text{I}^+$) possessing various substituents.

The following vinyl cations were examined: 1,2,2-tris(p-methoxyphenyl)vinyl cation ($\text{I}^+_1$), 1-p-methoxyphenyl-2,2-diphenylvinyl cation ($\text{I}^+_2$) and 1-p-methoxyphenyl-2,2-dimethylvinyl cation ($\text{I}^+_3$).

As expected, the nucleophilicity was found to depend strongly on the chemical nature of functional groups contained in the compounds under investigation. Moreover, it turned out that the electrophilicity of the vinyl cations was drastically improved by substituting aromatic groups in position 2 by methyl groups.

With respect to the present work it should be pointed out that, up to now, the reactivity of nucleophiles towards vinyl cations was examined only scarcely and that earlier work yielded only relative reactivities. Rappoport and Apeloig reported for instance [6] relative reactivities of some nucleophiles toward the 1,2-di-p-methoxyphenyl-2-phenylvinyl cation at 120 °C in acetic acid solution. The following relative reactivities (relative to \text{CH}_3\text{COO}^-) were given: \text{Br}^– (45.5), \text{Cl}^– (15.2), \text{CH}_3\text{COO}^- (1.0), \text{CH}_3\text{O}–\text{SO}_3^- (0.16) and \text{CH}_3\text{COOH} (0.0024).

Generation of Vinyl Cations

In earlier work substituted vinyl cations $\text{I}^+$ were generated by solvolysis of the corresponding halogen compounds $\text{I}$ [7].

$$\begin{align*}
\text{R}^1&\text{C}=\text{C}^+\text{R}^2 \\
\text{I}^+& + \text{Y} \rightarrow \text{Products}
\end{align*}$$

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were measured by recording the decrease of the optical absorption of $I^+$ as a function of time after the flash.

**Experimental Part**

**Materials**

Synthesis and purification of compounds $I_a$, $I_b$, and $I_c$ have been described elsewhere [10]. Compounds tested for nucleophilicity were commercial products (obtained from Aldrich or E. Merck). They were distilled prior to use. Olefinic compounds were freed from stabilizer by washing with aqueous sodium hydroxide solution. Acetonitrile was distilled from $P_2O_5$.

**Irradiations**

Acetonitrile solutions containing either $I_a$, $I_b$, or $I_c$ and a nucleophile (at varying concentrations) were irradiated in rectangular quartz cells with 20 ns laser flashes of 265 nm ($I_c$) or 347 nm light ($I_a$ and $I_b$). The absorption was ca. 20% and the absorbed dose per flash was ca. $1 \times 10^{-5}$ einstein/l. The concentrations of the substituted vinyl compounds were as follows: $2.9 \times 10^{-5}$ mol/l ($I_a$), $9.6 \times 10^{-5}$ mol/l ($I_b$), and $1.7 \times 10^{-5}$ mol/l ($I_c$).

Some of the experiments were carried out with Ar-saturated solutions, i.e. in the absence of $O_2$, others with air-saturated solutions. The same results were obtained in both cases indicating that $O_2$ does not react with vinyl cations.

**Results**

Fig. 1 shows typical oscilloscope traces obtained with compound $I_c$ demonstrating formation and decay of the optical absorption at 355 nm in the absence of additive. The decay of the absorption conformed to 1st order kinetics. If additives were present in the solution, the decay rate constant $k$ depended on the additive concentration $[Y]$ according to equation (3):

$$k = k_o + k_2[Y]$$

Here, $k_o$ is the decay rate constant measured in the absence of additive. Plots of $k$ vs. $[Y]$ yielded straight lines as can be seen from Fig. 2 where typical data are presented. Values of $k_2$ were obtained from the slopes of the straight lines. $k_2$ values are presented in Table I. Regarding single nucleophiles, the $k_2$ values obtained for the reactions of cation $I_c^+$ are about 20–55 times higher than those obtained for corresponding reactions of the cations $I_a^+$ and $I_b^+$. Obviously, cation $I_c^+$ is much more reactive than the cations $I_a^+$ and $I_b^+$. Moreover, $k_2$ values obtained for corresponding reactions of the cations $I_a^+$ and $I_b^+$ are equal within the error limit. Therefore, it is concluded that substitution of phenyl by anisyl does not bring about a change in the electrophilicity of the cations. However, substitution of aromating groups by methyl groups results in a significant increase in electrophilicity of the vinyl cation.

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**Fig. 1.** Flash photolysis of 1,2,2-tris($p$-methoxyphenyl)vinyl bromide in Ar-saturated acetonitrile solution ($2.9 \times 10^{-5}$ mol/l). Formation (a) and decay (b) of the optical absorption at $\lambda = 355$ nm during and after the 20 ns flash of 347 nm light. Absorbed dose per flash: $2 \times 10^{-3}$ einstein/l.

**Fig. 2.** Typical plots of observed pseudo 1st-order rate constants $k$ vs. the concentration of nucleophile (in this case tetrahydrofuran) according to eq. (3).

(a): $I_c^+$ ($1.7 \times 10^{-5}$ mol/l); $\lambda_{	ext{inc}} = 265$ nm.
(b): $I_b^+$ ($9.6 \times 10^{-5}$ mol/l); $\lambda_{	ext{inc}} = 347$ nm.
Table I. Rate constants $k_2$ (mol s$^{-1}$) of reactions of substituted vinyl cations, generated by flash photolysis of corresponding bromides, with various compounds in Ar-saturated acetonitrile solution at room temperature.

<table>
<thead>
<tr>
<th>Nucleophile</th>
<th>Vinyl cation</th>
<th>$k_2$ (mol s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1  N-Vinyl-2-pyrrolidone</td>
<td>An $\overset{\circ}{C}=\overset{\circ}{C}=\overset{\circ}{C}$</td>
<td>5.2 x 10$^4$</td>
</tr>
<tr>
<td>2  Styrene</td>
<td>Ph $\overset{\circ}{C}=\overset{\circ}{C}=\overset{\circ}{C}$</td>
<td>0.19 x 10$^4$</td>
</tr>
<tr>
<td>3  n-Butylvinylether</td>
<td>X $\overset{\circ}{C}=\overset{\circ}{C}$</td>
<td>0.71 x 10$^4$</td>
</tr>
<tr>
<td>4  $\alpha$-Methylstyrene</td>
<td>Me $\overset{\circ}{C}=\overset{\circ}{C}$</td>
<td>0.26 x 10$^4$</td>
</tr>
<tr>
<td>5  Methylmethacrylate</td>
<td>X $\overset{\circ}{C}=\overset{\circ}{C}$</td>
<td>0.12 x 10$^4$</td>
</tr>
<tr>
<td>6  Vinylacetate</td>
<td>X $\overset{\circ}{C}=\overset{\circ}{C}$</td>
<td>0.22 x 10$^5$</td>
</tr>
<tr>
<td>7  Acrylonitrile</td>
<td>Me $\overset{\circ}{C}=\overset{\circ}{C}$</td>
<td>unreactive**</td>
</tr>
<tr>
<td>8  N-Methyl-2-pyrrolidone</td>
<td>Ph $\overset{\circ}{C}=\overset{\circ}{C}=\overset{\circ}{C}$</td>
<td>3.4 x 10$^6$</td>
</tr>
<tr>
<td>9  Ethylbenzene</td>
<td>Ph $\overset{\circ}{C}=\overset{\circ}{C}=\overset{\circ}{C}$</td>
<td>unreactive**</td>
</tr>
<tr>
<td>10 Tetrahydrofuran</td>
<td>Ph $\overset{\circ}{C}=\overset{\circ}{C}=\overset{\circ}{C}$</td>
<td>5.7 x 10$^5$</td>
</tr>
<tr>
<td>11 Diethylether</td>
<td>Ph $\overset{\circ}{C}=\overset{\circ}{C}=\overset{\circ}{C}$</td>
<td>0.54 x 10$^6$</td>
</tr>
<tr>
<td>12 Methanol</td>
<td>Ph $\overset{\circ}{C}=\overset{\circ}{C}=\overset{\circ}{C}$</td>
<td>3.8 x 10$^8$</td>
</tr>
<tr>
<td>13 Ethanol</td>
<td>Ph $\overset{\circ}{C}=\overset{\circ}{C}=\overset{\circ}{C}$</td>
<td>3.2 x 10$^8$</td>
</tr>
<tr>
<td>14 2-Propanol</td>
<td>Ph $\overset{\circ}{C}=\overset{\circ}{C}=\overset{\circ}{C}$</td>
<td>1.2 x 10$^8$</td>
</tr>
<tr>
<td>15 t-Butanol</td>
<td>Ph $\overset{\circ}{C}=\overset{\circ}{C}=\overset{\circ}{C}$</td>
<td>1.8 x 10$^8$</td>
</tr>
</tbody>
</table>

With respect to the nucleophilicity of the compounds studied in this work, it is obvious that the benzene ring is unreactive. This results from a comparison of the $k_2$ values obtained with ethylbenzene, on the one hand, and those obtained with styrene and $\alpha$-methylstyrene, on the other hand.

**Discussion**

(i) **Nucleophilicity of various compounds**

**Pyrrolidones**

As can be seen from Table I N-methyl-2-pyrrolidone (8) exhibits a high reactivity toward vinyl cations if compared with the other compounds investigated in this work. The high reactivity of (8) seems to be caused by the rather pronounced nucleophilicity of the carbonyl oxygen giving rise to the attack of vinyl cations at the carbonyl groups:

Substitution of the methyl group by the vinyl group causes a reduction in $k_2$ by a factor of 6 to 7. Probably, this difference reflects the electron withdrawing power of the vinyl group causing a reduction in the nucleophilicity of the oxygen:

In connection with the interpretation given above it is interesting to refer to work of Alder [11, 12] on the methylation of a cyclic carbamate by methyl fluorosulphate. In this case the methylation at the carbonyl oxygen was reported to occur rapidly at room temperature:

**Esters**

The $k_2$ values of the esters 5 and 6 (1 to $2\times10^4$ l/mol s) are rather low and comparable to those of compounds possessing C–C double bonds but no oxygen such as 2 and 4. Obviously, the ester carbonyl group does not affect the nucleophilicity of 5 and 6. This is interpreted in terms of the electron withdrawing power of the ester oxygen:
Therefore, the nucleophilicity of the carbonyl oxygen is strongly reduced. Actually, this interpretation harmonizes with the findings and conclusion of Alder concerning the methylation of esters with the aid of methylfluorosulphate [11]. Methylacetate was not affected by FSO_3CH_3, and ethylacetate only to some extent which was attributed to the inductive effect being of importance in the case of esters.

**Ethers**

In the case of tetrahydrofuran (10) k_2 is appreciably higher than in the cases of diethylether (11) and n-butylvinylether (3). In accordance with the reactivity-selectivity principle the difference in k_2 values is higher in the cases of the less reactive cations I^c and I^a than in the case of the more reactive cation I^c. In the cases of I^c and I^a, k_2 values differ by about one order of magnitude, but with I^c they differ only by a factor of about four. The rather large differences in k_2 values are presumably explainable in terms of steric hindrance which makes a successful approach of a vinyl cation to the oxygen much less probable in the cases of 3 and 11 than in the case of 10.

**Alcohols**

k_2 Values obtained for methanol (12) are not very different from k_2 values found for tetrahydrofuran (10). Oxygen is considered being the reactive site in alcohols. By comparing k_2 values obtained with the alcohols 12–15, it is seen that k_2 is decreasing with increasing length of the carbon chain. This effect is explained in terms of steric hindrance becoming more important with alcohols having longer carbon chains.

**Olefinic compounds**

Carbons in phenyl groups are unreactive as was demonstrated by examining ethylbenzene (9). The lifetime of the vinyl cations was not affected by 9. In contrast, styrene (2) reduced the lifetime. Therefore, it is concluded that the C–C double bond is the reactive site in this case. However, the low value of k_2 (1.9×10^4 l/mol s) reflects a poor nucleophilicity. Similar values were found with α-methylstyrene (4), methylmethacrylate (5) and vinylacetate (6). The higher nucleophilicity observed with 1, and to some extent with 3, is attributed to the reactivity of oxygens contained in these compounds (vide ante). Acrylonitrile is quite unreactive, i.e., it does not differ from acetonitrile in its nucleophilicity. This might be due to the strong electron withdrawing power of the nitrile group which reduces largely the nucleophilicity of the C–C double bond.

(ii) **Electrophilicity of vinyl cations**

Since I_c does not absorb light at 347 nm, irradiations had to be carried out at 265 nm in this case. However, at this wavelength most of the compounds listed in Table I are not transparent. Rate constants k_2 of the reactions of I^c with N-methyl-2-pyrrolidone (8), tetrahydrofuran (10), diethylether (11) and various aliphatic alcohols (12–15) could be measured. They are 20–55 times higher than those obtained with I^a and I^c. As far as the alcohols are concerned, the dependence of k_2 on the number of carbon atoms is more pronounced in the case of I^c than in the case of I^a [9]. This is in accordance with the reactivity-selectivity principle according to which the more reactive carbocations react less selectively.

The high reactivity of I^c is probably due to the relatively high electron density at the carbons of the vinyl group and may also be attributed to some extent to steric hindrance effects being less pronounced in the case of I^c than in the cases of I^a and I^c. In this connection it is interesting to note that I^a and I^c exhibit almost no difference in k_2 values demonstrating almost equal electrophilicity.

Whereas the experiments of this work were carried out at Hahn-Meitner-Institut in Berlin, the manuscript was completed at the Faculty of Engineering of Hokkaido University in Sapporo, Japan. One of the authors (W. S.) wishes to express his gratitude toward the Hokkaido University and especially toward Prof. Dr. M. Katayama for an invitation as a special visiting professor.