

# Some Aspects of the Reactions of *ortho*-Quinodimethane Radical Cations and their Isomers in Gas-Phase Cycloaddition Reactions †

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The reactions of the radical cations of *ortho*-quinodimethane, styrene, and benzocyclobutene with ethene, propene and norbornadiene have been studied by FT-ICR spectrometry using an external ion source. The products of the ion-molecule reactions and the reaction efficiencies were determined.

The isomeric  $C_8H_9^+$  radical cations can be generated in the gas phase under carefully controlled conditions as stable, non-interconverting species. Styrene radical cations were produced directly from styrene by electron impact ionization or by charge exchange. *ortho*-Quinodimethane radical cations were generated by loss of  $H_2O$  from ionized 2-methylbenzyl alcohol or by electron impact ionization of benzocyclobutene. However, charge exchange of benzocyclobutene with toluene molecular ions produced mixtures of *ortho*-quinodimethane and benzocyclobutene radical cations. The latter ions are unreactive toward the alkenes studied (other than charge exchange).

The radical cations of styrene and *ortho*-quinodimethane are distinguished unambiguously by the rate constants of their reactions with alkenes and by the reaction products. The reaction of the styrene radical cations with propene are best explained by the formation of an intermediate open-chain adduct, which undergoes fragmentation in competition with cyclization to a [4+2] cycloadduct. All fragmentation products from the reactions of *ortho*-quinodimethane radical cations are derived from the [4+2] cycloadduct, suggesting either a concerted process or a fast two-step process. The difference between the reactivity of the radical cations of styrene and *ortho*-quinodimethane is particularly clear for the reaction with norbornadiene. Ionized styrene reacts predominantly by charge exchange while ionized *ortho*-quinodimethane forms mainly product ions by a [4+2] cycloaddition – [4+2] cycloreversion reaction sequence.

One of the most interesting reactions of alkene and alkadiene radical cations are radical cation mediated cycloadditions.<sup>1</sup> In particular, [4+2] cycloadditions of the Diels–Alder type are accelerated dramatically by the oxidation of one of the reactants to a radical cation. In these radical cation mediated reactions the  $[4\pi+2\pi]$  electron system of the cycloaddition is converted into either a  $[3\pi+2\pi]$  or a  $[4\pi+1\pi]$  electron system. It has been debated whether this will result in orbital symmetry forbidden and orbital symmetry allowed classes of reaction<sup>1,2</sup> but probably the activation barriers of both types are reduced so much that both reactions are observed, and probably both types of reaction follow a two-step mechanism.<sup>3</sup>

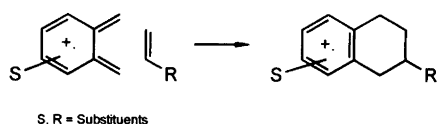
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Gas-phase studies of the reactions of radical cations permit the analysis of the reactivity and the reaction mechanisms of these highly reactive species. In the case of radical cation mediated cycloadditions the reactions of butadiene radical cations have been investigated by ion cyclotron resonance (ICR) spectrometry<sup>4</sup> and by tandem mass spectrometry using chemical ionization (CI).<sup>5</sup> These studies revealed the considerable reactivity of gaseous diene radical cations yielding cycloaddition products by a two-step mechanism involving distonic radical cations as intermediates generated in the addition step. Further, Chess *et al.*<sup>6</sup> have shown by tandem mass spectrometry, that *ortho*-quinodimethane (OQDM) and styrene (STY) produce 2-phenyltetralin in the plasma of a CI ion source via radical cations.

Reactions of OQDM radical cations with alkenes are particularly well suited to a more extended study of

gaseous  $[3\pi+2\pi]$  radical cation mediated reactions by FT-ICR spectrometry. The reactions restore the aromatic systems and are expected to be quite exothermic independent of substituents S and R present in the OQDM radical cations or in the alkene (Scheme 1). The ionization energy (IE) of OQDM of 7.70 eV<sup>7</sup> is sufficiently well below the IE of alkenes to prevent charge exchange (CE) from competing with radical cation mediated reactions. Thus, the tuning of the relative electronic and steric situation of the reactants should be possible by a variation of the substituents. Examination of the kinetics of these reactions by FT-ICR spectrometry is expected to give valuable information concerning the mechanisms of radical cation mediated reactions. With this intention an extended study of the reactions of OQDM radical cations and some other isomeric  $C_8H_8^{+\cdot}$  ions was started. In this paper, the first results are reported concerning mainly the reactions of the radical cations of OQDM and of the isomers STY and benzocyclobutene (BCB) with alkenes to ensure that any interconversion between these isomeric  $C_8H_8^{+\cdot}$  ions prior to or during their ion-molecule reaction will be detected and will not interfere with the analysis of the cycloaddition reactions.



Scheme 1.

## Experimental

All organic compounds used in the study were commercially available with the exception of benzocyclobutene (BCB), which was prepared according of Markgraf *et al.*<sup>8</sup>

For this study a Bruker CMS 47 X FT-ICR spectrometer equipped with a Bruker Spectrospin Infinity<sup>TM</sup> cell and an external EI/CI ion source was used. All mass spectra were recorded in the broad band mode (rf chirp excitation). The pressure readings for the ICR cell from

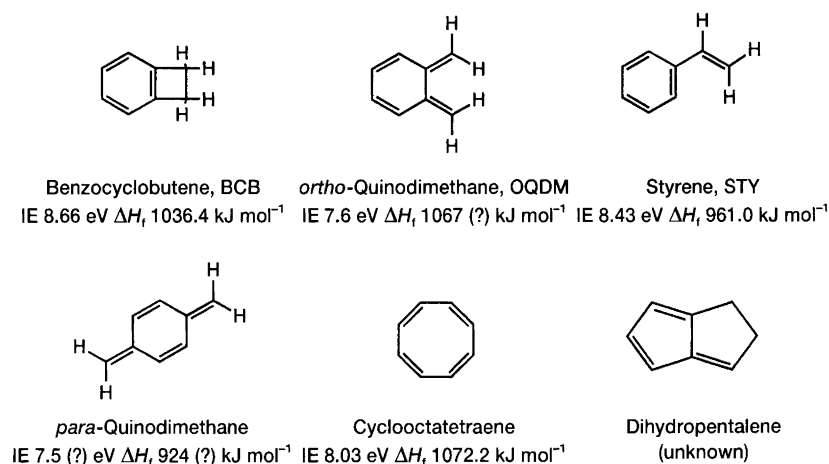
the ion gauge were first calibrated by using the rate constant  $k_{bi} = 1.5 \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  of the reaction<sup>9</sup>  $\text{CH}_4^{+\cdot} + \text{CH}_4 \rightarrow \text{CH}_5^+ + \text{CH}_3\cdot$  to correct for the different position of the ion gauge and the pumping system of the cell. Subsequently a second correction was applied for the different sensitivity of the ion gauge towards organic compounds used.<sup>10</sup> During all experiments the ICR cell was kept at room temperature.

The organic compounds used as precursors for the  $C_8H_8^{+\cdot}$  ions were introduced into the ion source by a probe inlet system at a suitable temperature, and were subjected to several freeze-pump-thaw cycles before introduction. The ions were generated in the external ion source by EI with 20–25 eV electrons or by CE with toluene (IE 8.82 eV<sup>11</sup>) as indicated. The neutral substrates were present in the FT-ICR cell as indicated for each experiment. For isolation of the reactant ions in the ICR cell after transfer from the ion source all ions except the reactant ions were ejected by a combination of a broad band rf pulse and short rf pulses at selected single frequencies to remove any remaining ions.

The pseudo-first-order rate constants  $k_{obs}$  were determined from the exponential decay of the reactant ions in the time-dependent mass spectra ('kinetic plots') by fitting the curve to a monoexponential decay function using the Origin 4.0 program.<sup>12</sup> The pseudo-first-order constants  $k_{obs}$  were transformed into second-order rate constants  $k_{bi}$  by dividing  $k_{obs}$  by the number density of the neutral molecules in the ICR cell. The reaction efficiency  $\text{eff} (\%) = k_{bi}/k_c \times 100$  of each process is calculated using the collision rate constant  $k_c$  obtained by the method of Su and Chesnavich.<sup>13</sup> The reproducibility of  $k_{obs}$  corresponds to  $\pm 10\%$ ; the absolute error of  $k_{bi}$  is about  $\pm 50\%$  because of the difficulties in the measurements of the partial pressure of the neutral reagent.

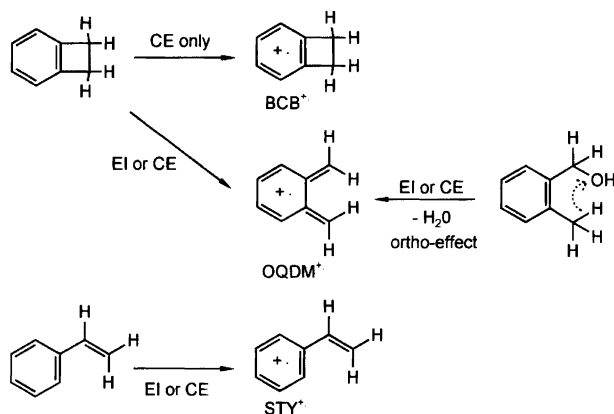
## Results and discussion

*Generation of  $C_8H_8^{+\cdot}$  radical ions.* The structures of the  $C_8H_8^{+\cdot}$  ions relevant to the present discussion are shown

Scheme 2.  $C_8H_8$  isomers.

in Scheme 2 together with the ionization energies, IE, of their neutral precursors,<sup>11</sup> and their heats of formation,  $\Delta H_f$ .<sup>11</sup>

The most stable  $C_8H_8^{+\cdot}$  species are the dihydropentadiene radical cation and  $STY^{+\cdot}$  ion, however, the  $\Delta H_f$  of the isomers are not very different. The interconversion of some of these  $C_8H_8^{+\cdot}$  ions in the gas phase<sup>14,15</sup> and in a solid matrix during radiolysis<sup>16</sup> has been studied before. Thus, it has been suggested that  $BCB^{+\cdot}$  ions isomerize spontaneously by electrocyclic ring opening into  $OQDM^{+\cdot}$  ions,<sup>15</sup> and that on radiolysis  $STY^{+\cdot}$  ions are also generated from  $BCB$ .<sup>16</sup> The  $STY^{+\cdot}$  ion and the  $OQDM^{+\cdot}$  ion are thought also to isomerize to the cyclooctatetraene radical cation before fragmentation.<sup>14</sup> In spite of this, the radical cations of  $OQDM$  and of  $STY$  have been created in the gas phase as stable non-interconverting species,<sup>6</sup> indicating that the isomerization is a high energy process of excited ions. However, as will be discussed below, these radical ions may interconvert during the reaction with alkenes. Thus, it is critical to generate  $OQDM^{+\cdot}$ ,  $STY^{+\cdot}$  and  $BCB^{+\cdot}$  ions under different experimental conditions as shown in Scheme 3 and to compare their reactions with the same alkenes as substrates to avoid any ambiguity in the interpretation of the reactions of  $OQDM^{+\cdot}$  ions.



Scheme 3. Generation of  $C_8H_8^{+\cdot}$  radical cations.

The  $STY^{+\cdot}$  ions are conveniently generated from  $STY$  by EI, and variations in the electron energy during EI have no effect on the behavior of these  $C_8H_8^{+\cdot}$  ions. The  $OQDM^{+\cdot}$  ions arise from elimination of  $H_2O$  from the molecular ions of 2-methylbenzyl alcohol by the so called *ortho* effect.<sup>17</sup> This reaction has been studied carefully<sup>18</sup> and yields conclusively  $OQDM^{+\cdot}$  ions as the sole product ions. Again, neither variation in the electron energy during EI nor formation of the 2-methylbenzyl alcohol molecular ions by CE has an effect on the behavior of the resulting  $C_8H_8^{+\cdot}$  ions.  $C_8H_8^{+\cdot}$  ions exhibiting the properties of  $OQDM^{+\cdot}$  were also obtained by EI of  $BCB$  with an electron energy  $> 12$  eV. However,  $BCB^{+\cdot}$  ions have to be formed primarily by this ionization method and there may be a chance that at least some of the  $BCB^{+\cdot}$  ions survive if the ionization process is more gentle. Hence,  $BCB$  was also ionized by CE with

toluene (IE = 8.82 eV,<sup>11</sup>) yielding indeed a mixture of  $C_8H_8^{+\cdot}$  ions. Finally, it should be noted for the discussion of the reactions of these  $C_8H_8^{+\cdot}$  ions that all ions were produced in the external ion source of the FT-ICR spectrometer and transferred to the FT-ICR cell for reaction. The time that elapsed between then and the start of the kinetic experiment was at least 1 s. Hence, it is very unlikely that the ions in this phase of the experiment contained excess electronic and vibrational energy for isomerization. Any interconversion of the  $C_8H_8^{+\cdot}$  ions must have occurred during the ionization process in the ion source.

**Reactions with ethene.** Ion-molecule reactions of  $OQDM^{+\cdot}$  ions (from EI-induced loss of water from 2-methylbenzyl alcohol) and  $STY^{+\cdot}$  ions with ethene are very slow and can be observed only at relatively high pressures of ethene ( $> 10^{-6}$  mbar) in the FT-ICR cell and at long reaction times. An ion intensity vs. reaction time diagram ('kinetic plot') of these reactions is shown in Fig. 1. Under the conditions employed the reaction of  $STY^{+\cdot}$  ions with ethene was complete after 200 s, and a reaction efficiency of 0.024% was calculated from the disappearance of the  $STY^{+\cdot}$  ions,  $m/z$  104. The main reaction product is an adduct ion  $C_{10}H_{12}^{+\cdot}$ ,  $m/z$  132, which fragments into the secondary product ions

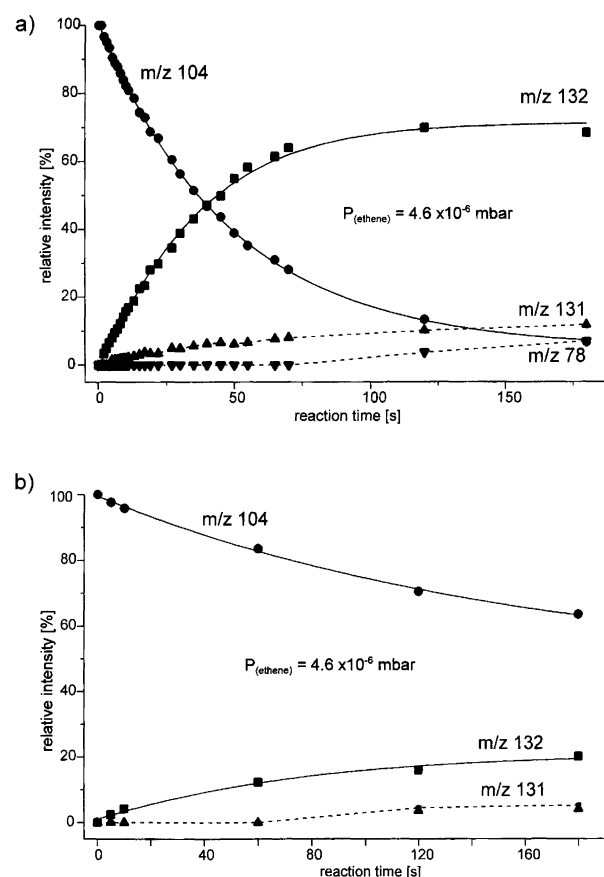


Fig. 1. Kinetic plot for the reactions of (a)  $STY^{+\cdot}$  and of (b)  $OQDM^{+\cdot}$  with ethene.

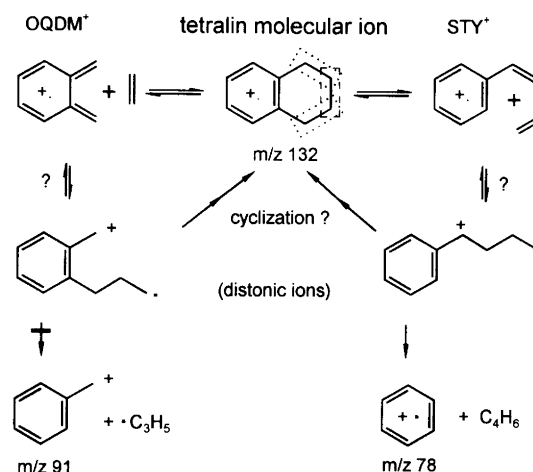
$C_{10}H_{11}^{+\cdot}$ ,  $m/z$  131, and  $C_6H_6^{+\cdot}$ ,  $m/z$  78. The ion  $C_{10}H_{12}^{+\cdot}$ ,  $m/z$  132, may correspond to tetralin, which would be the product of the [2+4] cycloaddition reaction of  $STY^{+\cdot}$  ions with ethene, or to phenylcyclobutene radical cation as the [2+2] product, or to an open-chain distonic ion. The reaction of  $OQDM^{+\cdot}$  ions, generated by the different methods mentioned above, with ethene is even less efficient than that of  $STY^{+\cdot}$  ions and could not be followed to completion.

At a partial pressure of ethene of  $4.5 \times 10^{-6}$  mbar only about 40% of the ions  $OQDM^{+\cdot}$  reacted after 200 s, corresponding to a reaction efficiency  $<0.01\%$ . The main product is again the adduct ion  $C_{10}H_{12}^{+\cdot}$ ,  $m/z$  132, but this time only  $C_{10}H_{11}^{+\cdot}$  ions,  $m/z$  131, were observed as secondary product ions.

The very small efficiencies obtained for the reactions of  $STY^{+\cdot}$  ions and  $OQDM^{+\cdot}$  ions with ethene in the FT-ICR spectrometer cannot be interpreted in terms of the insignificant reactivity of these ions towards cycloadditions. Ion-molecule reactions in dilute gas phase exhibit, in most cases, a double well or multiple well potential energy hypersurface<sup>19</sup> and occur in a collision complex energetically excited by the attractive electrostatic forces between ionic and neutral reactants. Furthermore, in the special case of an exothermic addition reaction the adduct ions are also excited by chemical activation. This excess energy of the addition product ions results in a fast reaction in the forward direction by fragmentation or in the reverse direction by dissociation into the reactants. A fast forward reaction of the excited product ion resulting in a large experimental rate constant or efficiency of the total reaction requires an exothermic fragmentation. If there is no exothermic reaction channel available in the forward direction the excited adduct ion dissociates back to reactants in competition with stabilization by collisional deactivation. In an FT-ICR spectrometer this latter process is slow, however, because of the low pressure in the FT-ICR cell. In this case the experimental efficiency is small and is determined by the efficiency of the collisional deactivation of the adduct ion, which is then observed as the main reaction product. This is obviously the genuine situation in the case of the reactions of  $STY^{+\cdot}$  and  $OQDM^{+\cdot}$  ions with ethene since the loss of a hydrogen atom is not an energetically favorable fragmentation. In fact, hydrogen loss cannot compete with the elimination of  $C_2H_4$  from metastable tetralin molecular ions,<sup>20</sup> which are the expected products of cycloaddition. Hence, most of the adduct ions,  $m/z$  132, formed during the reaction dissociate into  $C_2H_4$  and  $C_8H_8^{+\cdot}$  ions,  $m/z$  104, and only some are collisionally stabilized if the pressure in the FT-ICR cell is sufficiently high.

According to these arguments the efficiencies measured for the reactions of  $STY^{+\cdot}$  and  $OQDM^{+\cdot}$  ions with ethene correspond to the rate of the collisional deactivation of the adduct ions,  $m/z$  132. Interestingly, the efficiencies are different for both reactions in spite of a nearly identical background pressure of propene, and for

the adduct ion from  $STY^{+\cdot}$  ion and ethene collisional deactivation can compete more efficiently with back dissociation. It is not very likely that the rate constants of deactivation of  $C_{10}H_{12}^{+\cdot}$  ions differ by nearly a factor of two, and a more probable explanation is a reduced rate constant for the back dissociation of the  $STY^{+\cdot}$  adduct ion, thereby increasing the lifetime of the adduct ion. This can be explained by the initial formation of an open-chain distonic ion by the addition of an  $STY^{+\cdot}$  ion to ethene. This distonic ion rearranges quickly by hydrogen migration in competition with eventual cyclization to tetralin molecular ions (Scheme 4). Such a distonic intermediate and its rearrangement by hydrogen migration also explains the competing dissociation into benzene molecular ion  $C_6H_6^{+\cdot}$ ,  $m/z$  78, and neutral butadiene. For the reverse reaction of benzene radical cations with butadiene it has been shown that the adduct ion,  $m/z$  132, corresponds to an open-chain distonic ion.<sup>21</sup>



Scheme 4. Reaction scheme of  $OQDM^{+\cdot}$  ions or  $STY^{+\cdot}$  ions with ethene.

In this connection it is of interest to note that no fragment ions other than  $m/z$  131 are observed for the reaction of  $OQDM^{+\cdot}$  ions with ethene. Clearly, the formation of benzene molecular ions,  $m/z$  78, is not possible by hydrogen rearrangements only from the distonic intermediate of this reaction. Instead, hydrogen rearrangements followed by loss of a  $C_3H_5$  radical should yield the stable  $C_7H_7^+$  ion, which is not observed, however. This indicates that either the terminating cyclization to give the tetralin molecular ion of the distonic ion generated by addition of a  $OQDM^{+\cdot}$  ion to ethene is fast compared with any rearrangement or that the product ion of the cycloaddition is produced directly without a distonic intermediate.

Finally, it should be recalled that metastable tetralin molecular ions eliminate  $C_2H_4$  by two competing mechanisms (Scheme 4) resulting in  $OQDM^{+\cdot}$  ions,  $m/z$  104, by cycloreversion, and in  $STY^{+\cdot}$  ions,  $m/z$  104, by a more complicated but energetically more favorable process.<sup>22</sup> Thus, formation of an excited tetralin molecular ion by a radical cation mediated cycloaddition reaction

of these ions with ethene and subsequent fragmentation may result in the interconversion of OQDM<sup>+</sup> and STY<sup>+</sup> ions catalyzed by ethene. In the present experiment this isomerization is not detected and would require reactions of isotopically labeled reactants. However, this interconversion becomes obvious during the reactions of OQDM<sup>+</sup> and STY<sup>+</sup> ions with propene.

**Reactions with propene.** The kinetic plots of the reactions of OQDM<sup>+</sup> (from EI-induced loss of water from 2-methylbenzyl alcohol) and STY<sup>+</sup> ions with propene are shown in Fig. 2. The efficiencies of 3.4% for OQDM<sup>+</sup>

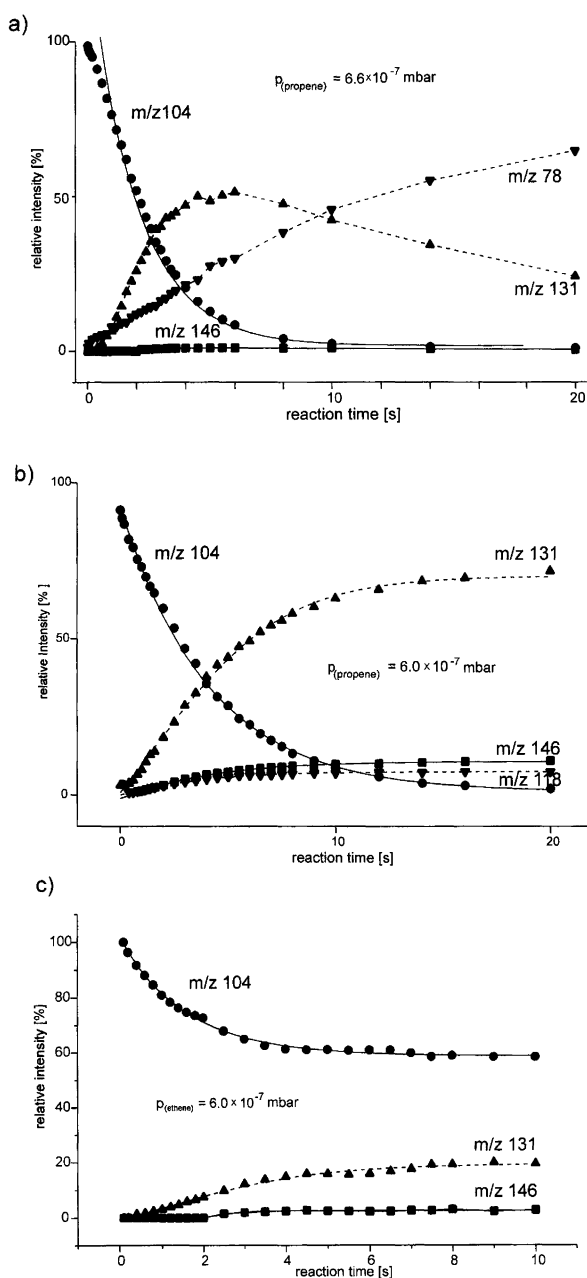


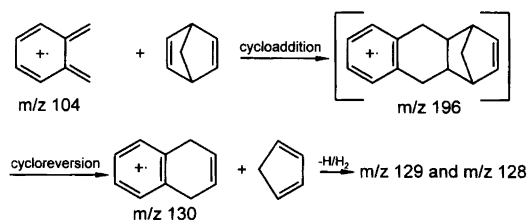
Fig. 2. Kinetic plot for the reactions of (a) STY<sup>+</sup>, of (b) OQDM<sup>+</sup>, and of (c) a mixture of OQDM<sup>+</sup> and BCB<sup>+</sup> with propene.

ions and of 5.4% for STY<sup>+</sup> ions signify again rather slow processes that, however, are more than two orders of magnitude faster than with ethene as a substrate. For both reactions the main product is C<sub>10</sub>H<sub>11</sub><sup>+</sup> ion, *m/z* 131, arising from the adduct ion C<sub>11</sub>H<sub>14</sub><sup>+</sup>, *m/z* 146, by loss of a methyl radical. This fragmentation is distinctly more favorable than the loss of H<sup>•</sup> and therefore enhances the fragmentation of the excited adduct ion, *m/z* 146, which is detected with minor intensity only.

In the case of the reaction of STY<sup>+</sup> ions, the benzene ions C<sub>6</sub>H<sub>6</sub><sup>+</sup>, *m/z* 78, are a second abundant product. The relative intensity of the ions *m/z* 78 increases with reaction time at the expense of the ions *m/z* 131 indicating the formation of the benzene ions not only by fragmentation of a distonic intermediate of *m/z* 146, but also by a further reaction of the product ions *m/z* 131. No such reaction and no formation of ions *m/z* 78 is observed during the reaction of OQDM<sup>+</sup> ions with propene. Instead, a second fragmentation product of the adduct ion *m/z* 146 appears at *m/z* 118, corresponding to ions C<sub>9</sub>H<sub>10</sub><sup>+</sup>. Interestingly, this is the second fragment ion besides C<sub>8</sub>H<sub>8</sub><sup>+</sup>, *m/z* 104, expected for the fragmentation of the cycloaddition product 2-methyltetralin molecular ion by competing losses of ethene and propene (Scheme 4),<sup>15</sup> corroborating the interconversion of OQDM and STY type ions by a reversible reaction of these ions with alkene. Further, the formation of product ions C<sub>6</sub>H<sub>6</sub><sup>+</sup>, *m/z* 78, only in the reaction of STY<sup>+</sup> ions with propene confirms unequivocally the formation of a distonic adduct ion in this reaction as an intermediate in line with the reaction model discussed before and illustrates again the different reactivities of OQDM<sup>+</sup> and STY<sup>+</sup> ions towards alkenes.

In further experiments with propene as the substrate the ions C<sub>8</sub>H<sub>8</sub><sup>+</sup> were generated from BCB by EI ionization or by CE with toluene (IE = 8.82 eV). In the first case the kinetic plots were identical with those of OQDM<sup>+</sup> ions produced by water elimination from ionized 2-methylbenzyl alcohol [Fig. 2(b)]. However, in the second case kinetic plots exhibiting bimodal kinetics for the reactions of the ions C<sub>8</sub>H<sub>8</sub><sup>+</sup> are obtained [Fig. 2(c)] in which one component reacts very slowly or not at all with propene. This component corresponds very likely to the BCB<sup>+</sup> ion, which exhibits no reactivity towards cycloaddition. The relative concentration of the BCB<sup>+</sup> ions depends very much on the experimental conditions of the preparation, though. Obviously, the interconversion of BCB<sup>+</sup> and OQDM<sup>+</sup> ions requires only a modest activation energy. Nevertheless, these reactions of C<sub>8</sub>H<sub>8</sub><sup>+</sup> ions with propene confirm the expectation that the isomeric ions STY<sup>+</sup>, BCB<sup>+</sup>, and OQDM<sup>+</sup> can be generated as stable species in the gas phase under carefully controlled conditions and can be distinguished by their reactions with alkenes.

**Reactions with norbornadiene.** Neutral OQDM reacts smoothly with norbornadiene by a Diels–Alder reaction, and the EI mass spectrum of the Diels–Alder product



Scheme 5. Reaction scheme of OQDM<sup>+</sup> ions with norbornadiene.

exhibits a very intense signal due to the elimination of cyclopentadiene from the molecular ion.<sup>23</sup> An analogous fragmentation from an intermediate product ion is expected if OQDM<sup>+</sup> ions react with norbornadiene in a radical cation mediated cycloaddition reaction (Scheme 5).

The kinetic plots for the reactions of STY<sup>+</sup> and OQDM<sup>+</sup> ions with norbornadiene are shown in Fig. 3 and the composition of the reaction mixture after the C<sub>8</sub>H<sub>8</sub><sup>+</sup> ions have disappeared is listed in Table 1. The IE of norbornadiene of 8.35 eV<sup>11</sup> is below that of STY (IE = 8.43 eV<sup>11</sup>) and the STY<sup>+</sup> ions react by CE with norbornadiene. Thus, the ionic reaction products arise from a further reaction of norbornadiene radical cations. This has been certified by an independent experiment.

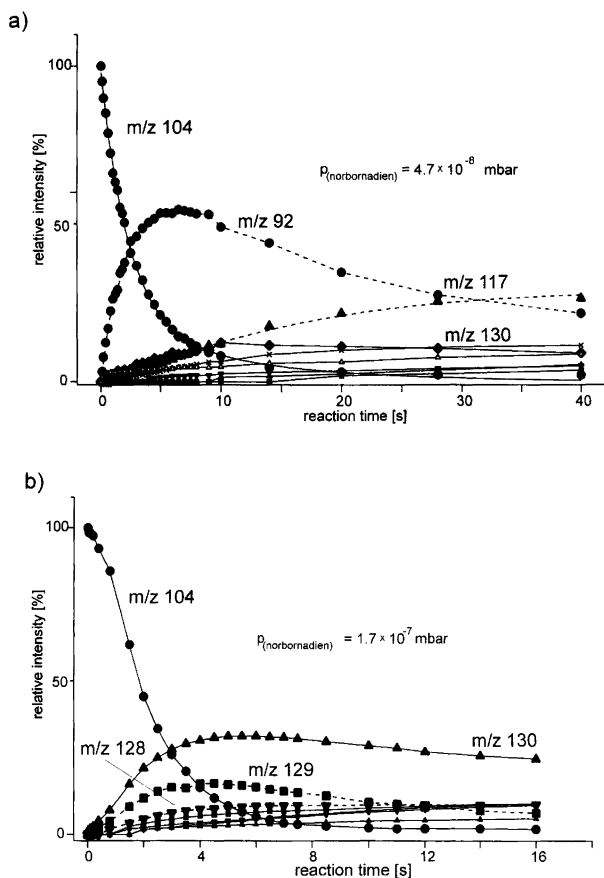


Fig. 3. Kinetic plot for the reactions of (a) STY<sup>+</sup> and of (b) OQDM<sup>+</sup> with norbornadiene.

Table 1. Relative intensity of product ions at the end of the reaction of ions STY<sup>+</sup>, OQDM<sup>+</sup>, and norbornadiene<sup>+</sup> with norbornadiene.

Product ion <i>m/z</i>	STY <sup>+</sup> rel. int. (%)	OQDM <sup>+</sup> rel. int. (%)	Norbornadiene <sup>+</sup> rel. int. (%)
209			3.1
193			2.6
181	12.0	10.0	6.7
169			3.4
168		5.2	3.4
167	16.8	9.5	14.7
155	12.2	10.1	9.8
143			7.2
142		4.7	
141			0.6
131		9.5	5.7
130	10.4	24.6	2.0
129		7.0	2.5
128		9.9	
119	7.0		5.5
118	9.3		6.6
117	11.7	7.6	9.0
104	5.8	1.8	
92	1.9		11.5
91	11.6		5.2

The OQDM<sup>+</sup> ions also produce a complex mixture of product ions by reaction with norbornadiene, but no CE occurs and the most prominent product ions appear at *m/z* 130, *m/z* 129 and *m/z* 128, accounting for about 50% of the final product ions (Table 1). The ion *m/z* 130 corresponds to the expected product ion C<sub>10</sub>H<sub>10</sub><sup>+</sup> of the cycloaddition–cycloreversion sequence shown in Scheme 5. Obviously, this ion still contains some excess energy and releases one and two hydrogen atoms generating stable naphthalenium ions, *m/z* 129, and naphthalene radical cation, *m/z* 128.

These reactions of C<sub>8</sub>H<sub>8</sub><sup>+</sup> ions with norbornadiene thus not only confirm the existence of stable isomeric C<sub>8</sub>H<sub>8</sub><sup>+</sup> ions under the conditions of FT-ICR spectrometry but support convincingly the high reactivity of OQDM<sup>+</sup> radical ions towards cycloaddition. In the reactions of OQDM<sup>+</sup> ions with the alkenes studied here all product ions can be derived from energetically excited [4+2] cycloaddition products without the intervention of open-chain distonic ions as intermediates. Although this does not prove unambiguously a concerted [3 $\pi$ +2 $\pi$ ] process for these gas-phase reactions, the final cyclization of a two-step mechanism must be very fast to prevent any other competing rearrangement or fragmentation.

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