

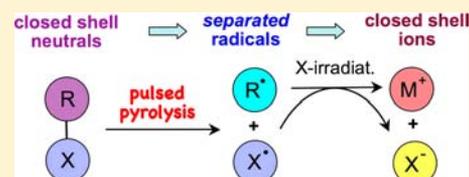
Carbocations Generated under Stable Conditions by Ionization of Matrix-Isolated Radicals: The Allyl and Benzyl Cations

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S Supporting Information

ABSTRACT: Carbocations are crucial intermediates in many chemical reactions; hence, considerable effort has gone into investigating their structures and properties, for example, in superacids, in salts, or in the gas phase. However, studies of the vibrational structure of carbocations are not abundant, because their infrared spectra are difficult to obtain in superacids or salts (where furthermore the cations may be perturbed by counterions), and the generation of gas-phase carbocations in discharges usually produces several species. We have applied the technique of ionizing neutral compounds by X-irradiation of cryogenic Ar matrices to radicals embedded in such matrices, thus producing closed-shell cations that can be investigated leisurely, and in the absence of counterions or other perturbing effects, by various forms of spectroscopy. This Article describes the first set of results that were obtained by this approach, the IR spectra of the allyl and the benzyl cation. We use the information obtained in this way, together with previously obtained data, to assess the changes in chemical bonding between the allyl and benzyl radicals and cations, respectively.



INTRODUCTION

Understanding the structure and the properties of reactive intermediates can help to clarify the mechanisms of reactions where these intermediates are involved. Carbonium ions¹ are a class of reactive intermediates, which are of considerable importance in different organic reactions (electrophilic additions and substitutions, S_N1 and $E1$ reactions, etc.).² A variety of carbocations have therefore been studied by means of NMR and UV spectroscopy in superacids,³ and occasionally also their salts with nonnucleophilic anions by crystallography.⁴ However, much less is known about the vibrational structure of carbocations because superacid solutions cannot easily be probed by IR spectroscopy.

Carbocations can also be generated in the gas phase, either by passing the precursors through an electric or microwave discharge⁵ or by protonation.⁶ The vibrational structure of cations may then be probed, for example, by multiphoton or double resonance infrared photodissociation (IRPD) spectroscopy, techniques that have yielded much valuable insight into the vibrational structure of many charged species. Different electronic states of carbocations can be observed by photoelectron spectroscopy of the corresponding radicals.^{7,8} By threshold ionization and/or detection of zero-kinetic-energy electrons (ZEKE), even vibrational states of closed-shell cations can be detected at high resolution.⁹ Finally, it should be mentioned that high-lying Rydberg states of radicals show properties that are very similar to those of the core cations,¹⁰ which may be exploited to learn about the vibrational structure of carbocations.

When carbocations occur as intermediates in nature, they are often formed by oxidation of radicals.¹¹ It occurred to us that this approach might also be used to make closed-shell cations in the condensed phase in a targeted fashion and, if they can be

generated under stable conditions, to probe them by different forms of spectroscopy.

In the 1980s, we had developed a technique for ionizing neutral, closed-shell molecules embedded in cryogenic Ar matrices by X-irradiation to form radical cations, which could then be probed leisurely by “classical” UV/vis and IR absorption spectroscopy.^{12,13}

An extension of this technique to ionize radicals, in view of forming closed-shell cations, is readily conceivable, but the implementation of this idea requires a suitable source of radicals. Often, radicals probed by matrix isolation spectroscopy are generated by UV photolysis of suitable precursors, but the disadvantage of this approach is that radicals are invariably created in pairs that are trapped within the same matrix cavity where they can (and often will) recombine, if not right after their creation, then most probably after ionization in Ar, which invariably results in some excess energy being imparted on the resulting cations.

If, however, radicals are generated by pyrolysis, they will be trapped in different sites of a matrix when the effluent of the pyrolysis tube is condensed on a cold window. Two different pyrolytic techniques are available: *flash vacuum pyrolysis*,¹⁴ where the precursors are energized by collisions with the walls of a pyrolysis tube (and can in principle recombine or undergo other bimolecular reactions in the gas phase), and *pulsed pyrolysis* of a precursor embedded in a large excess of an inert host gas¹⁵ (Ar in our case), where activation occurs by collisions with hot Ar atoms and where bimolecular reactions are very unlikely to occur. We decided to use the latter

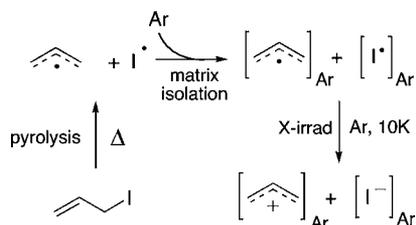
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technique, because it has proven particularly suitable for the generation of radicals.¹⁶

As our targets are presently carbocations, we used iodides R–I to form radicals R• and iodine atoms I• because the latter serve as excellent scavengers of the electrons which are produced in the subsequent X-irradiation of the Ar matrix, thus leaving the holes to travel through the matrix and be trapped by the radicals R• to selectively form cations R⁺, as shown in Scheme 1 for R = allyl, which we chose to serve as a proof of principle. We then went on to investigate the benzyl cation about which, despite it being a textbook case of a resonance stabilized carbocation, surprisingly little is known.

Scheme 1. Generation of the Allyl Cation



As the spectra of the radicals and their corresponding cations are now available from the same experiment, this allows one to probe the changes in chemical bonding upon ionizing radicals, changes that, in the case of the allyl and the benzyl radical, were expected to be subtle at most, because ionization occurs from a nonbonding orbital, shown in Figure 1.

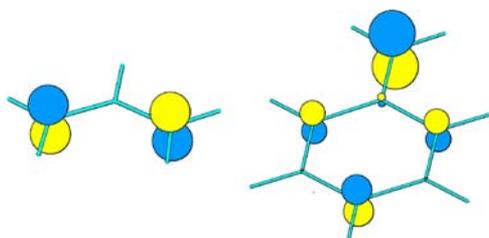


Figure 1. The singly occupied molecular orbitals (SOMOs) of the allyl and the benzyl radical.

To use the information contained in the vibrational spectra of the radicals and the cations to assess the changes in chemical bonding, a valence force field has to be established. We used for this purpose a procedure introduced by Pulay et al. in the 1980s whereby a force field calculated by a quantum chemical method is transformed into valence coordinates and scaled such as to obtain optimal agreement between calculated and observed frequencies.¹⁷ The resulting valence force constants can then be compared, for example, between different oxidation states of a compound, as we had done it previously with butadiene and its radical cation.¹⁸

RESULTS

The Allyl Cation. To obtain the required vibrational spectra, we thus generated the allyl radical by pulsed pyrolysis of allyl iodide in a 1000-fold excess of Ar (see Materials and Methods), trapped the outflow of the pyrolyzer on a 10 K CsI plate, and exposed the resulting Ar matrix to X-irradiation. IR spectra were measured before and after X-irradiation, and their difference shows downward pointing peaks for species that go

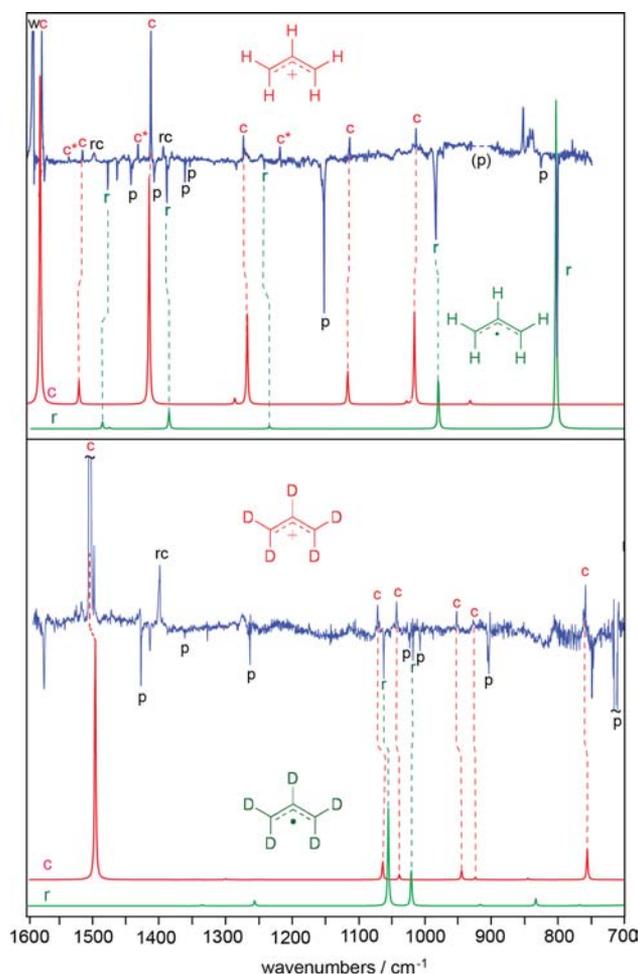


Figure 2. Experimental difference spectra (blue) for the ionization of the allyl radical, and calculated IR spectra for the H₃ or D₃ radicals (green), and for the corresponding cations (red), respectively. The bands in the experimental spectra are labeled “r” (radical), “c” (cation), “p” (unpyrolyzed allyl iodide precursor), “rc” (allyl iodide radical cation), and “w” (matrix-isolated water). Dashed lines denote correlations between calculated and observed peaks (peaks labeled c* are assigned to combination bands, cf., Table 1).

away and upward pointing peaks for species that are newly formed in the course of the irradiation. In the present case, the IR difference spectra shown in Figure 2 illustrate the conversion of the allyl radical and of some of the leftover allyl iodide into the allyl cation and some allyl iodide radical cation, respectively. The identity of the bands of the allyl iodide and its radical cation was assessed in separate experiments without pyrolysis.

All bands that we attribute to the allyl radical and its perdeuterated isotopomer, labeled by a green “r”, correspond exactly to those that Nandi et al. had observed under similar experimental conditions,¹⁹ so there can be no doubt about the identity of this species. Most of the peaks that arise on ionization of the H₃ isotopomer turn out to be in good accord with those observed recently by IRPD spectroscopy of the allyl cation in Ar and N₂ clusters,²⁰ and/or as vibrational progressions in high-resolution photoelectron spectra of the allyl radical.⁹ Some additional bands in the protio- and five bands in the deuterio species can be assigned to the allyl cation on the basis of the excellent agreement with the frequencies and intensities obtained from a scaled valence force field (Table 1, see Materials and Methods for details of the procedure).

Table 1. Calculated and Experimental Frequencies (in cm^{-1}) of the Allyl Cation

species	normal modes		calcd ^a frequencies (intensities)	experimental frequencies		
	numbering ^b	symmetry ^c		this work	Douberly et al. ²⁰ (N_2/Ar)	Gasser et al. ⁹ (PES)
C_3H_5^+	ν_{11}	b_1	1016.1 (44)	1013	–/1025	1009(2)
	ν_{10}	b_1	1116.3 (17)	1113	1136/1130	1111(2)
	$\nu_{18}+\nu_{12}$	a_1	[1234] (–)	1218 ^d	1226/1230	
	ν_{17}	b_2	1268.2 (44)	1273	1278/1278	1276(2)
	ν_{16}	b_2	1416.1 (107)	1412	1418/1421	
	$\nu_{11}+\nu_7$	b_1	[1450] (–)	1432 ^d		
	ν_4	a_1	1522.0 (11)	1516		
	$\nu_{10}+\nu_7$	b_1	[1556] (–)	1535 ^d		
	ν_{15}	b_2	1580.6 (174)	1577	1581/1585	
C_3D_5^+	ν_{11}	b_1	756.1 (32)	758		
	ν_{10}	b_1	925.4 (3)	927		
	ν_{17}	b_2	946.3 (10)	952		
	ν_5	a_1	1040.0 (5)	1042		
	ν_{16}	b_2	1065.3 (20)	1071		
	ν_{15}	b_2	1500.4 (276)	1505		

^aHarmonic frequencies from a scaled valence force field based on a B3LYP/6-31G* calculation; intensities are in km/mol, rounded to integers.

^bFundamentals are numbered consecutively from higher to lower frequencies within each irreducible representation, the order of which is a_1 , a_2 , b_1 , and b_2 . ^cAssuming that the C_2 -axis is the z axis and the x -axis is perpendicular to the molecular plane. ^dCombination bands; calculated frequencies are the sum of those for the constituent fundamentals.

In the spectra of both isotopomers, there are also some decreasing bands that cannot be attributed to allyl radical or allyl iodide (e.g., the peaks at 1575 and at 1420 cm^{-1} in C_3D_5) and increasing bands that cannot be assigned to the allyl cation or the radical cation of allyl iodide (e.g., the peak at 850 cm^{-1} in C_3H_5). They may stem from secondary decomposition products or impurities that arise on pyrolysis.

Of the nine IR-active fundamentals that group theory and DFT calculations predict to occur in the range that we observe in our experiments (500–2000 cm^{-1}), we can assign six each for the H_5 and for the D_5 allyl cation (the three others having very low predicted intensities; all of the fundamentals are listed in the Supporting Information). In contrast to Douberly et al.,²⁰ we prefer to assign the band at 1273 cm^{-1} to the fundamental, ν_{17} , predicted at 1268 cm^{-1} , and that at 1218 cm^{-1} to a combination band, predicted (in the harmonic approximation) at 1234 cm^{-1} . The fundamental ν_4 at 1516 cm^{-1} had not been detected by Douberly et al., and we observed two new bands (at 1432 and 1535 cm^{-1}), which we assign to combination bands according to our calculations (see Table 1).

The Benzyl Cation. Despite its exemplary nature, surprisingly little is known experimentally about the parent benzyl cation. Even its UV spectrum has been a matter of debate until recently: while some studies advocated a single absorption at ca. 360 nm,^{21,22} others reported a strong band peaking at ca. 310 and a weak one at 460 nm.^{23,24} Only in 2011 has it become possible to assign the 460 nm band unambiguously to the benzyl cation isolated in a Ne matrix,²⁵ so this question is now settled (we have observed the same band in our experiments described below).

Many fundamentals and combination bands of the benzyl cation and two deuterated isotopomers were observed in the 1990s by the group of Weisshaar using first ZEKE photoelectron²⁶ and later threshold photoionization spectroscopy.²⁷ However, these studies missed out on most of the fundamentals that were predicted by calculations to occur above 1200 cm^{-1} . Thus, we decided to subject the benzyl cation to the same scrutiny as the allyl cation, in the hope of complementing the above information.

The benzyl radical was produced by pyrolysis of benzyl iodide, and so was its D_7 isotopomer. The frequencies for the H_7 radical agree very well with those reported in 1993 by Baskir et al.,²⁸ except that we observed four additional fundamentals (13 in total) and a combination band.

In the D_7 isotopomer of the benzyl radical, which has not been described before, we were able to assign 14 out of 21 fundamentals that are predicted to occur in our observation range. Details of the vibrational structure of the benzyl radical will stand at the focus of a forthcoming separate paper.

On X-irradiation of the resulting Ar matrices, the difference spectra shown in Figure 3 were obtained. As in the above case of the allyl system, a group of bands emerges that can be assigned quite unambiguously to the benzyl cation, while a few others are attributable to the benzyl iodide radical cation (the bands of the benzyl iodide that remains after pyrolysis also decrease on X-irradiation).

A problem in the benzyl case is that the strongest band of the cation coincides with the (unavoidable) sharp peaks of matrix-isolated water molecules, which are partly complexed to the substrate molecules and which therefore change slightly in frequency on ionization of that substrate. We have tried to pinpoint this strong peak of the benzyl cation by careful inspection of the similarities and the subtle differences in spectra from a series of experiments. This has led us to the conclusion that the peak at 1629 cm^{-1} in the protio species and that at 1586 cm^{-1} in the deuterated isotopomer should be attributed to the benzyl cation.

In Table 2, the frequencies of the fundamentals of the benzyl cation reported in 1996 by Weisshaar²⁷ and those observed in the present study are juxtaposed to the ones calculated by the scaled quantum chemical force field method (see Discussion). For the protio compound, this allows us to assign 24 of the 29 IR-active fundamentals that are predicted to occur below 2000 cm^{-1} , 11 of which had not been observed previously. For the D_7 isotopomer, 15 fundamentals could be assigned with confidence (of which five are new ones). It is satisfactory to note that the three fundamentals that were observed both in our and in the previous gas-phase study²⁷ are within a few

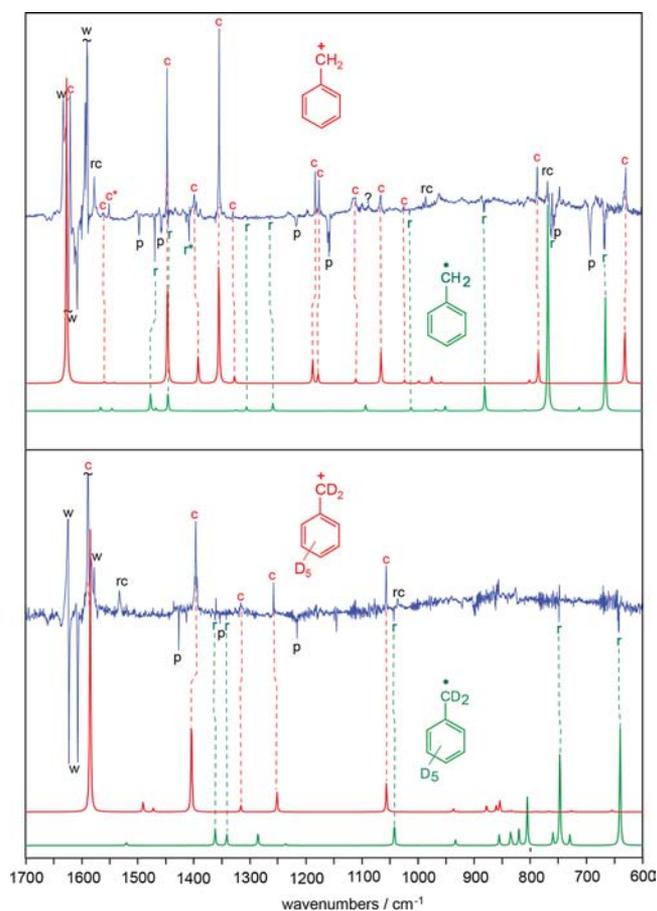


Figure 3. Experimental difference spectra (blue) for the ionization of the benzyl radical, and calculated IR spectra for the H₇ or D₇ radicals (green), and for the corresponding cations (red), respectively. The bands in the experimental spectra are labeled “r” (radical), “c” (cation), “p” (unpyrolyzed benzyl iodide precursor), “rc” (benzyl iodide radical cation), and “w” (matrix-isolated water). Dashed lines denote correlations between calculated and observed peaks (the peak labeled r* is assigned to combination band, cf., Table 2 in the Supporting Information).

cm⁻¹, and that the two sets of experiment give almost perfectly complementary information.

DISCUSSION

Let us recall that one of the goals of this study was to see whether the chemical bonding changes upon ionization of the allyl and benzyl radicals, notwithstanding the fact that ionization occurs in both cases from a nonbonding π -molecular orbital (cf., Figure 1). As we shall see, there is more to it than this simple view reveals.

One way to address the question would be to see how vibrational frequencies shift on ionization. Yet if ionization does affect the vibrational structure, then the normal modes that are associated with the vibrational frequencies change also; that is, they cannot be directly compared between the radicals and their corresponding cations. As a consequence, shifts in frequencies cannot be directly translated into chemically useful information. What *can* be compared between similar structures are the *force constants* for bond stretches, angular deformations, and out-of-plane distortions.²⁹

In the 1980s, Pulay et al. introduced a procedure to transform the harmonic Cartesian force fields that are

Table 2. Calculated and Experimental Frequencies (in cm⁻¹) of the Benzyl Cation

species	normal modes		calcd ^a frequencies (intensities)	experimental frequencies	
	numbering ^b	symmetry ^c		this work	ref 27
C ₇ H ₇ ⁺	ν_{24}	b ₁	162 (6)		163
	ν_{17}	a ₂	337 (0)		316
	ν_{36}	b ₂	354 (2)		353
	ν_{23}	b ₁	410 (1)		400
	ν_{13}	a ₁	524 (4)		525
	ν_{35}	b ₂	598 (2)		598
	ν_{16}	a ₁	626 (0)		627
	ν_{22}	b ₁	631 (46)	630	
	ν_{21}	b ₁	783 (24)	787	
	ν_{12}	a ₁	803 (3)	804	820
	ν_{34}	b ₂	965 (1)		973
	ν_{10}	a ₁	999 (2)	993	1008
	ν_{19}	b ₁	1030 (3)	1025	
	ν_{18}	b ₁	1068 (25)	1067	
	ν_{33}	b ₂	1112 (4)	1112	1115
	ν_{32}	b ₂	1179 (9)	1178	1183
	ν_9	a ₁	1189 (19)	1187	
	ν_{31}	b ₂	1329 (6)	1330	
	ν_8	a ₁	1360 (105)	1355	
	ν_{30}	b ₂	1393 (23)	1399	
ν_{29}	b ₂	1448 (89)	1448		
ν_{28}	b ₂	1544 (1)		1547	
ν_6	a ₁	1565 (2)	1561		
ν_5	a ₁	1630 (250)	1624		
C ₇ D ₇ ⁺	ν_{24}	b ₁	145 (5)		145
	ν_{17}	a ₂	286 (0)		278
	ν_{36}	b ₂	302 (1)		302
	ν_{23}	b ₁	360 (2)		349
	ν_{13}	a ₁	498 (4)		500
	ν_{35}	b ₂	574 (2)		575
	ν_{12}	a ₁	728 (2)		737
	ν_{34}	b ₂	771 (1)		779
	ν_{32}	b ₂	859 (8)		862
	ν_9	a ₁	942 (4)		951
	ν_8	a ₁	1064 (30)	1057	
	ν_7	a ₁	1252 (20)	1258	
	ν_{30}	b ₂	1315 (7)	1313	
	ν_{29}	b ₂	1404 (102)	1397	
	ν_5	a ₁	1586 (288)	1590	

^aHarmonic frequencies from a scaled valence force field based on a B3LYP/6-31G* calculation; intensities are in km/mol, rounded to integers. ^bFundamentals are numbered consecutively from higher to lower frequencies within each irreducible representation, the order of which is a₁, a₂, b₁, and b₂. ^cAssuming that the C₂-axis is the z-axis and the x-axis is perpendicular to the molecular plane.

calculated by quantum chemical programs into force fields for a set of valence coordinates.¹⁷ The purpose was to fit calculated to experimental spectra by optimizing a set of factors by which different types of valence force constants were scaled, as opposed to the scaling of all calculated frequencies by a single factor, as it was (and still is) customary in the field. By this approach, a better agreement between experiment and calculation can indeed be reached, and it has often helped to achieve unambiguous assignments of vibrational transitions.

On the other hand, such scaling confers a measure of physical reality to the computed valence force constants, and therefore

also to their comparison between different molecules. This is especially true because methods have meanwhile become available that reproduce experimental spectra quite well, even without much scaling, which means that the force fields from these methods are very likely to be physically reasonable to begin with (as a matter of fact, Pulay's method has largely fallen into disuse because it is no longer needed to arrive at correct assignments of most vibrational spectra).

We therefore decided to apply this method to the present case; that is, we transformed the force fields for the allyl and benzyl radicals and cations that were calculated by the B3LYP/6-31G* method into a set of valence coordinates according to the rules provided by Pulay et al.,¹⁷ which we separated into six or seven groups (see Materials and Methods). Each group was scaled separately so as to minimize the root-mean-square deviation between all observed and calculated frequencies. The discussion below will focus on those valence force constants that are of most chemical interest and that undergo the largest changes on ionization. The full force fields are given in the Supporting Information.

The Allyl Radical/Cation. As Table 3 shows, some of the diagonal valence force constants change quite considerably between the allyl radical and the allyl cation, which indicates surprisingly strong differences in chemical bonding (we shall not attempt to interpret the small changes for the in-plane bending and the C–CH₂ torsional modes, because these may well be within the error limits of the B3LYP method or the scaling model).

Table 3. Diagonal Valence Force Constants of the Allyl Radical and Cation^a

valence deformation	C ₃ H ₅ [•]	C ₃ H ₅ ⁺	change in %
C–C stretch	6.204	7.244	+16.8
CH ₂ scissor	0.446	0.485	+4.3
CH ₂ rock	0.508	0.536	+5.6
C–H bend (ip) ^b	0.536	0.536	+0.6
C–C–C bend	1.065	1.126	+5.4
C–H wag (oop) ^b	0.296	0.235	–20.4
CH ₂ pyramid	0.175	0.323	+97.7
C–CH ₂ torsion	0.270	0.292	+7.4

^aStretching force constants are in aJ/Å² (=mdyn/Å), and those for angular deformations are in aJ/rad² (=mdyn·Å/rad²). ^bip = in-plane, oop = out-of-plane.

The most pronounced changes occur for the pyramidalization of the CH₂ groups where the force constant nearly doubles on ionization. This comes as no surprise, as methyl radicals are much easier to pyramidalize than methyl cations: the frequency of the umbrella mode increases from 606 cm^{–1} in the methyl radical³⁰ to 1404 cm^{–1} in the methyl cation.³¹

Conversely, the force constant for the central C–H wagging mode decreases by 20% on ionization of the allyl radical, which cannot be an artifact, because the corresponding force constant is defined to >50% by the observed vibrations (see the Supporting Information). We can currently offer no “chemical” explanation for this intriguing feature.

Another unexpected change involves the (spectroscopically also well founded) 16.8% increase of the C–C stretching force constant on ionization of the allyl radical. To explain that, it turns out to be judicious to consider the *off-diagonal element* of the force constant matrix, which represents the interaction of the two C–C stretches. This element is much larger in the allyl

radical than it is in the cation (1.37 vs 0.56 aJ/Å²), which makes the force constants for the symmetric and the antisymmetric combinations of C–C stretches differ much more in the former case.³²

Thus, one finds that the force constant for the *symmetric* stretching deformation changes insignificantly on ionization, whereas that for the *antisymmetric* stretching increases by 38% (from 4.836 to 6.685 aJ/Å²). The reason for this strong change of the latter force constant is that the antisymmetric stretch corresponds to a deformation of b₂ symmetry, which optimally couples the ²A₂ ground state of the allyl radical to its low-lying ²B₁ excited state. The resulting pseudo-Jahn–Teller effect leads to a flattening of the potential surface for this deformation (i.e., a lowering of the force constant) in the ground state, and a corresponding increase in the curvature in the excited state.³³

The same effect does not come to bear as clearly in the other symmetrized valence deformations of b₂ symmetry (the antisymmetric combinations of the CH₂ scissoring and rocking deformations), because these modes are much less effective in coupling the ¹2A₂ and the ¹2B₁ states. This expresses itself in tiny off-diagonal force constants for these two pairs of deformations.

The Benzyl Radical/Cation. Twenty-seven of the 36 valence force constants for the benzyl system involve deformations of the C₆H₅ ring and of the hydrogen atoms that are attached to it. These force constants contain little “chemically useful” information, and they change in fact insignificantly on ionization. The values for the remaining force constants, which all involve the exocyclic C–CH₂ group, are listed in Table 4. All of these force constants are very well-defined by the available spectroscopic information, including that provided in the 1990s by the Weisshaar group.^{27,34}

Table 4. Some Diagonal Valence Force Constants of the Benzyl Radical and Cation, Which Involve the Exocyclic C–CH₂ Moiety^a

valence deformation	C ₇ H ₇ [•]	C ₇ H ₇ ⁺	change in %
>C–CH ₂ stretch	5.709	7.700	+35
>C–CH ₂ rock (ip) ^b	0.833	0.795	–4.6
>C–CH ₂ wag (oop)	0.562	0.281	–50.1
>C–CH ₂ torsion ^b	0.242	0.379	+56.6
–CH ₂ scissor (ip)	0.448	0.469	+4.7
–CH ₂ rock (ip)	0.516	0.539	–4.6
–CH ₂ wag (oop)	0.146	0.315	+115.5

^aStretching force constants are in aJ/Å² (=mdyn/Å), and those for angular deformations are in aJ/rad² (=mdyn·Å/rad²). ^bip = in-plane, oop = out-of-plane.

As in the above case of the allyl radical, the force constants for in-plane C–H deformations change less than 5% on ionization, while that for wagging (pyramidalization) of the CH₂ group more than doubles on going to the cation (the effect is even larger than in the allyl radical, presumably because of the higher spin density on that CH₂ group in the benzyl radical). Interestingly, the force constant for torsion around the C–CH₂ bond also increases by nearly 60%, in line with the increase of the rotational barrier (from 11 kcal/mol in the benzyl radical to 45 kcal/mol in the benzyl cation, according to G4 calculations, cf., Supporting Information). The reason for this increase may be that it takes more energy to formally localize a charge than an unpaired electron on the exocyclic CH₂ group.

Another marked change is that for the C–CH₂ out-of-plane wagging motion, the force constant of which decreases by almost 50%. As in the similar case of the wagging of the central H-atom in the allyl system, the force constant of which also decreases markedly on ionization, we can presently offer no convincing “chemical” rationale for this feature, but we hope that our study will incite someone to come up with an explanation.

CONCLUSION

We have presented a new method to generate closed-shell cations in Ar matrices by ionization of the corresponding radicals, which are in turn generated by pulsed pyrolysis of iodides. The electrons and the holes that are formed on subsequent X-irradiation of the resulting Ar matrices are scavenged by the iodine atoms and the (spatially separated) organic radicals, respectively, which makes that the targeted cations can be studied as isolated species that are unperturbed by counterion or solvent effects. As solid Ar is transparent from the UV to the far IR, this approach makes it possible to probe both the precursor radicals and the corresponding cations in the same experiment by electronic and vibrational spectroscopies. The method is general in that it can be applied to all radicals/cations for which precursors with a labile bond can be made.

We have applied this method to study the allyl and the benzyl radicals and cations, respectively. We used the information obtained from our IR spectra of the protio- and the perdeuterated isotopomers of each species, and from previous gas-phase studies, to scale a force field in the same valence coordinates for each precursor radical and its cation. This allowed us to examine the changes in bonding on oxidation of the radicals. As the electron that is removed on oxidation comes from a nonbonding orbital, one expects these changes to be minimal. However, we found that several of the valence force constants change by surprisingly large amounts. We offer “chemical” rationales for most of these changes, although some of them remain unexplained.

MATERIALS AND METHODS

Syntheses. The iodide precursors were made from the corresponding alcohols (which are commercially available, both in the protio and in the perdeuterated forms) by reaction with HI, using a slightly modified form or the procedure described by Klein et al.³⁵ In the case of the allyl alcohol, we simply added 1.7 equiv of HI (and no phosphoric acid) and left the mixture at room temperature, which resulted, after meticulous purification, in a ca. 10% yield of allyl iodide. In the case of the benzyl alcohol, we found that we had to heat the same mixture to 130 °C in a microwave oven to get the reaction to go. The yields of the benzyl iodides after purification were 80% or more.

Pulsed Pyrolysis Matrix Isolation. The details of our pulsed pyrolysis apparatus will be described in a forthcoming publication. Briefly, a mixture of the iodide with Ar was passed at ca. 200 Torr through a pulsed valve and pyrolyzed in a ca. 4 cm long SiC tube (ID = 1 mm) held at ca. 800 °C in the case of allyl iodide, and 950 °C in the case of benzyl iodide. The yields of radicals were optimized with the help of a time-of-flight mass spectrometer as described by Zhang et al.¹⁶ The resulting molecular beam was trapped on a CsI plate held at 10 K in a closed-cycle cryostat. IR spectra were recorded by a Bomem DA3 interferometer at 0.5 cm⁻¹ resolution.

Ionization. Ionization was effected by exposing the Ar matrices containing the radicals and iodine atoms to X-rays emanating from a tungsten target tube operated at 40 kV/40 mA. This leads to the formation of electron–hole pairs in the Ar matrix.³⁶ Because of its high electron affinity, the iodine atoms trap most of the electrons, which

leaves the holes to diffuse through the matrix until they are trapped by the easily oxidizable radicals. At the same time, allyl or benzyl iodide molecules that survived the pyrolysis is also ionized, but the identities of the bands of these radical cations can be established in separate experiments.

Computational Methods. Cartesian force constants were calculated by the B3LYP/6-31G* method as implemented in the Gaussian 09 program system.³⁷ We tried several of the more “modern” functionals (M06, B2PLYP, and others) and larger basis sets, but B3LYP/6-31G* invariably gave the best accord with experiment after scaling the frequencies by a single factor. Therefore, we decided to use the B3LYP force field as a basis for the scaled valence force field.

The above force fields were transformed into a nonredundant set of internal coordinates using the SCALE2 program of Pulay et al.¹⁷ For the purpose of scaling, we grouped all force constants for (a) C–C stretches, (b) C–C–C bends, (c) C–H bends, (d) C–H out-of-plane wags, (e) CH₂ pyramidalization, and (f) C–C torsion. For the benzyl system, we additionally separated the CH₂ scissoring and rocking mode from the ring C–H bends, and we assigned a separate scaling factor to C–CH₂ out-of-plane wag. The C–H stretching force constants were invariably left unscaled and were not used in the analysis.

To scale the force fields of the radicals, we used mainly the frequencies from the present matrix isolation experiments. In the case of the allyl radical, those vibrational frequencies reported by Nandi et al.,¹⁹ which we did not observe, were used in addition, if they were predicted to within less than 15 cm⁻¹ by the valence force field. Thereby, we discovered some assignments of weak bands that are probably erroneous, because the difference between the predictions of the scaled force field and the reported frequencies is beyond what can be expected. In the case of the allyl cation, it was gratifying to note that the optimized force field reproduced the low frequencies observed in the gas phase by Gasser et al.⁹ within a few wavenumbers, with the exception of the lowest one, which is probably a very anharmonic distortion. Details of this will be reported in a forthcoming publication.

The definition of the valence coordinates, the full force fields in these coordinates, and an analysis of all normal modes in terms of the potential energy distribution over the valence coordinates are given in the Supporting Information. Note that one has to exercise care and circumspection when one applies a scheme with multiple scaling factors, to avoid artifacts due to underdetermination. However, ample previous experience with this method^{18,38} has taught us how to avoid such pitfalls.

ASSOCIATED CONTENT

Supporting Information

(a) Figures and tables showing the definition of the valence coordinates, (b) an Excel spreadsheet containing the full results of the scaled force field calculations (all calculated and observed frequencies, and full force constant matrix and potential energy distribution of all normal modes in terms of the valence coordinates), and (c) geometries and energies of all of the species discussed in this work (pdf file, containing also the full quotation of ref 23). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

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- (32) To obtain the force constants for the symmetric and the antisymmetric C–C stretching deformations, one simply has to add or subtract the off-diagonal element for the coupling of the two modes to or from the diagonal elements, respectively.
- (33) It has never been attempted to pinpoint the frequency of a b_2 vibration that prominently involves the antisymmetric C–C stretch in the richly structured weak first absorption band of the allyl radical (Tonokura, K.; Koshi, M. *J. Phys. Chem. A* **2000**, *104*, 8456). However, according to CASSCF(3,3)/TZV calculations, the frequency of that vibration increases from 1165 cm^{-1} in the ground state (1177 cm^{-1} according to our scaled force field) to 1764 cm^{-1} in the first excited state (cf., Tonokura and Koshi), which is a strong indication that the potential surface for the antisymmetric C–C stretching is indeed much steeper in the excited state than in the ground state.
- (34) After careful scaling of the force field, two fundamentals that were proposed by Eiden et al.²⁷ showed significantly larger deviations from the predicted values than any of the others, which may hint toward a misassignment. We therefore removed these two modes (that reported at 316 cm^{-1} in the protio compound, which is off by 20 cm^{-1} , and that reported at 349 cm^{-1} in the perdeuterated isotopomer) from the scaling procedure. After that, the combined root-mean-square deviation between all calculated and observed fundamentals of both isotopomers dropped to 4.5 cm^{-1} , a very satisfactory value.
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