Polynes such as retinal, carotene, and antimycotic agents are common natural pigments due to their extended π-electron systems that enable visible light to induce bright π-π* transitions. In many cases, these transitions lead to structural changes as the π* excited-state character promotes rotation about the polylene backbone. The best-known example is the retinal protonated Schiff base, which undergoes photoisomerization within the ops protein and initiates the first step in the visual phototransduction cycle. The retinal protonated Schiff base chromophore can undergo many photoisomerization and thermal reversion cycles in the protein; however, as an isolated cation, it may degrade through intramolecular cyclization. Similar isomerization processes are also known to occur in isolated polylene anions, for example, following collisional activation. However, direct photoinduced isomerization of anionic polyenes have not been studied, in part because direct photodetachment (i.e., instantaneous light-induced electron ejection) is an open channel and one might anticipate that the electron will simply leave. However, it is well-established that π* resonances can often complicate the photoelectron spectroscopy of bright chromophore anions, particularly in polyaromatic and highly conjugated systems, where photoexcitation to resonances can be much more probable than direct photodetachment. The dynamics of such resonances can have striking effects on the measured photoelectron spectra because ultrafast excited-state nuclear motion can compete with autodetachment. These effects can take the form of changing Franck-Condon factors, internal conversion dynamics, or dissociation dynamics leading to an anionic fragment from which an electron is subsequently photodetached. Several recent photoelectron studies on conjugated anions have shown that photoexcitation of resonances followed by ground electronic state recovery is a very efficient process. Alternatively, dissociation can occur directly on the potential energy surface of the resonance if it is repulsive or from the ground electronic state provided that there is an efficient internal conversion route and the total vibrational energy exceeds the bond dissociation energy. In the latter case, the dissociation products can provide insight into ground-state chemical transformations. Because ground-state isomerization reactions can occur in polylene anions and because internal conversion can compete with autodetachment, one might also expect polylene anions to undergo cyclization reactions following photoexcitation.

In the present photoelectron imaging study, we show that UV excitation (hν = 4.13 eV) of the deprotonated polyeneic acid anion, octatrienoic acid, [C7H5–CO2]–, leads to the formation of both [C7H5]– and the hydride anion, H−. We adapt the photoelectron velocity-mapping conditions to allow direct imaging of H−, which exhibits a Boltzmann-like kinetic energy release distribution. Combining all experimental evidence with supporting electronic structure calculations, we...
propose a two-step mechanism. First, photoexcitation of a resonance at \( h\nu = 4.13 \text{ eV} \) leads to excited-state dissociation of \( \text{CO}_2 \) to produce ground electronic state \([\text{C}_7\text{H}_9]^-\). Next, the vibrationally hot \([\text{C}_7\text{H}_9]^-\) undergoes an intramolecular cyclization to form toluene and \( \text{H}^- \). Our results demonstrate that anion resonances can lead to rich photochemistry and that the combination of photoelectron imaging and charged-particle imaging is a useful tool for probing the intermediates and products of unimolecular anion reactions.

Experimentally, \([\text{C}_7\text{H}_9-\text{CO}_2]^-\) (Figure 1) was generated by electrospray ionization, mass-selected and intersected with laser pulses (\( \sim 5 \text{ ns duration} \)) at 4.13 eV (300 nm) or 4.66 eV (266 nm) at the center of a perpendicular velocity-map imaging (VMI) spectrometer.\(^{23,24}\) The VMI spectrometer has been optimized to perform photoelectron spectroscopy by gating the imaging detector with a \( \sim 100 \text{ ns gate pulse} \) and reconstructing the raw image.\(^{25}\) However, the same perpendicular VMI spectrometer can also be used to image other charged species, such as \( \text{H}^- \). Supporting ground electronic structure calculations were performed at the G4 level of theory and resonance energetics computed at the multistate XCMQDPT2 level of theory.\(^{26,27}\)

The photoelectron spectra of \([\text{C}_7\text{H}_9-\text{CO}_2]^-\) taken at \( h\nu = 4.13 \text{ and } 4.66 \text{ eV} \) are shown in Figure 1a,b, respectively. The photoelectron spectra are dominated by a peak at low electron kinetic energy, \( e\text{KE} \), which is generally indicative of the indirect electron loss process of thermionic emission.\(^{15,20,28,29}\) In addition to this low \( e\text{KE} \) peak, there are several minor features at higher \( e\text{KE} \). In the \( h\nu = 4.13 \text{ eV} \) spectrum, the low \( e\text{KE} \) peak has a shoulder that extends up to \( \sim 1.4 \text{ eV} \) and a weak feature that peaks at \( e\text{KE} \approx 2.5 \text{ eV} \), as indicated by the asterisk in Figure 1a. The photoelectron spectrum at \( h\nu = 4.66 \text{ eV} \), shown in Figure 1b, is broadly similar, although the shoulder to the dominating low \( e\text{KE} \) peak is larger than that at \( h\nu = 4.13 \text{ eV} \) and extends to \( e\text{KE} \approx 1.9 \text{ eV} \), which is consistent with a direct photodetachment process. The \( h\nu = 4.66 \text{ eV} \) spectrum does not, however, show the clear peak at around \( e\text{KE} \approx 2.5 \text{ eV} \) (or at \( e\text{KE} \approx 3.0 \text{ eV} \) taking into account the additional photon energy).

In addition to the peak at \( e\text{KE} \approx 2.5 \text{ eV} \) in the \( h\nu = 4.13 \text{ eV} \) photoelectron spectrum, a discernible peak is present at \( e\text{KE} \approx 3.3 \text{ eV} \), as indicated by the arrow in Figure 1a. The peak is more clearly seen in the magnified photoelectron spectrum in Figure 2a and the raw photoelectron image in Figure 2b. Unlike the other features at lower \( e\text{KE} \) that are all isotropic in the photoelectron image, the photoelectron feature corresponding to the peak at \( e\text{KE} \approx 3.3 \text{ eV} \) is highly anisotropic (\( \beta \approx \pm 2 \)), corresponding to electron ejection parallel to the laser polarization axis, \( \epsilon \).\(^{30}\) Furthermore, the peak width is close to the velocity-mapping resolution (\( \sim 0.17 \text{ at } 3.3 \text{ eV} \)), which is surprising considering the molecular size of \([\text{C}_7\text{H}_9-\text{CO}_2]^-\) and that the anions were initially thermalized to 300 K in the ion trap. Sharp photoelectron features have been observed in anion photoelectron spectra of large molecules, where they have been found to correspond to weakly bound nonvalence orbitals such as dipole-bound states.\(^{31}\) However, \textit{trans}-[\text{C}_7\text{H}_9-\text{CO}_2]^- has a calculated dipole moment of 1.7 D, which is insufficient to support a dipole-bound state.\(^{32}\) Moreover, the binding energy (\( \epsilon \text{BE} = h\nu - e\text{KE} \)) is inconsistent with a weakly bound nonvalence orbital. In the present case, the narrow peak has a binding energy of \( \sim 0.8 \text{ eV} \), which is close to the known electron affinity of \( \text{H} \) at 0.75497 eV (the electron affinities of C or O are inconsistent with the observed binding energy).\(^{33}\) In addition, the angular anisotropy associated with this peak suggests that the outgoing wave has angular momentum of \( l = 1 \) (p-wave), which is expected for photodetachment of an electron from the 1s orbital (\( l = 0 \)) of \( \text{H}^- \).\(^{30}\) We therefore assign the narrow feature to result from \( \text{H}^- \) photodetachment, which must be first dissociated from \([\text{C}_7\text{H}_9-\text{CO}_2]^-\). Therefore, this two-photon detachment process must occur within the duration of the 5 ns laser pulse.

To further characterize the dissociation mechanism, we performed VMI of the \( \text{H}^- \) product. Ground-state dissociation involves internal vibrational energy redistribution, which occurs on a picosecond time scale, prior to the excess energy being statistically imparted into the relevant modes to induce bond cleavage.\(^{34}\) If this mechanism is in operation, the kinetic energy release associated with the \( \text{H}^- \) fragment should exhibit a Boltzmann-like distribution. Additionally, the angular distribution associated with \( \text{H}^- \) dissociation may be expected to be isotropic because molecular rotation is much faster than statistical unimolecular dissociation. In contrast, prompt
excited-state dissociation may be expected to produce H− with a high (non-Boltzmann) and potentially anisotropic kinetic energy release distribution. Such dynamical behavior is well-known for excited-state H atom dissociation.35 Although the present experiment was not designed to characterize ion fragments, our arrangement still allowed the H− product to be imaged, albeit offset from the center along the propagation axis of the ion beam because of the perpendicular VMI arrangement and the mass (time-of-flight) difference between an electron and H−.

To velocity-map H−, we extended the imaging acquisition gate on the multichannel plate (MCP) from 100 ns to 1 μs to account for the much longer time-of-flight of H− compared with that of photoelectrons. Figure 2c shows a raw photoelectron image of [C7H9−CO2]− taken at hv = 4.13 eV with a MCP gate of 1 μs and a VMI voltage of 1500 V (which is three times that used for photoelectron imaging). The photoelectron image can be identified in Figure 2c, although is reduced in radial extent due to the higher VMI voltages. The tail-like signal observed to the left of this image arises from delayed photoelectron emission over the 1 μs MCP gate width; after a few 100 ns, the main ion packet has moved out of the interaction region and the VMI condition is no longer maintained, leading to a smearing out of the photoelectron signal at the opposite side of the emission point. This effect was confirmed with SIMION simulations and is visible because of the extended gate of the MCP detector.36 The slow electron loss shows that electrons are still “boiling off” the vibrationally hot [C7H9−CO2]− over the gate time scale, which is consistent with the assignment that the low eKE feature in the photoelectron spectra is a result of thermionic emission (statistical electron ejection) from the anion ground electronic state.15,20,28,29 Thus, the main product channel following photoexcitation of [C7H9−CO2]− at hv = 4.13 or 4.66 eV is recovery of the ground electronic state, showing that resonances must be excited at both energies.

In addition to the photoelectron signal in the velocity-map image in Figure 2c, there is signal arising from dissociated H− impacting the MCP detector. The offset of the center of the H− image relative to the photoelectron image provides a velocity calibration for the kinetic energy release distribution of H−. Specifically, the velocity vector of H−, v, is the same as that of the original [C7H9−CO2]− beam, determined to be |v| ≈ 4.8 × 104 m s−1 from its time-of-flight. This velocity is proportional to the offset in camera pixels of the photoelectron image center and the H− image center (assuming that the photoelectron center is the true zero-velocity center of the spectrometer). To analyze the H− fragment, the image was centered onto the H− photodetachment feature, reconstructed using polar-onion peeling, and calibrated to yield the kinetic energy release spectrum in Figure 2d. The H+ kinetic energy release exhibits a broad and unstructured peak that closely resembles a Boltzmann distribution (dashed line in Figure 2). The tendency away from the Boltzmann curve at higher kinetic energy is due to overlap with the electron signal from the parent ion beam. Additionally, as shown in Figure 2c, the angular distribution of the H− fragment is isotropic. In summary, the Boltzmann-like and isotropic kinetic energy distribution of H− suggest a statistical ground electronic state dissociation process.

The electronic structure calculations identified two optically active π* resonances, summarized in Figure 3, that are accessible in our experiments. The first resonance at ~4.2 eV (oscillator strength of ~0.2) involves charge transfer of a π orbital localized on the CO2 group to π* orbitals on the polyene. The second resonance at ~4.5 eV (oscillator strength of ~1.0) involves π* ← π transitions on the polyene.

Direct photodetachment from [C7H9−CO2]− can be identified in Figure 1 by the features extending to 1.4 or 1.9 eV in the hv = 4.13 and 4.66 eV spectra, respectively. By extrapolating the high-eKE edge of this feature, the adiabatic binding energy of [C7H9−CO2]− was determined to be 2.6 ± 0.1 eV. The direct photodetachment peak at both hv = 4.13 and 4.66 eV is small compared with thermionic emission, suggesting that ground-state recovery is very efficient. Indeed, our calculations support that π* resonances are photoexcited at both photon energies; therefore, similar to other aromatic anions15,20 there must be efficient internal conversion to the electronic ground state. The VMI supports that H− formation occurs through a ground electronic state dissociation process. However, such a mechanism is inconsistent with the fact that H− loss is only observed at hv = 4.13 eV and not at hv = 4.66 eV, suggesting that there must be a specific photoexcitation and excited-state process (i.e., two-step mechanism) that leads to the observed differences.

Additional insight can be gained by considering the photoelectron feature indicated by the asterisk in Figure 1a, which extends up to eKE ≈ 2.9 eV. On the basis of the 1.27 ± 0.03 eV electron affinity of heptatriene, C7H9, determined by Brauman and co-workers,37 this feature can be assigned to direct photodetachment of [C7H9]− by a second (sequential) photon from the ~5 ns laser pulse. Thus, the hv = 4.13 eV spectrum indicates that CO2 is lost very rapidly following excitation of [C7H9−CO2]−. A similar [C7H9]− photodetachment feature is not observed at hv = 4.66 eV, suggesting that CO2 is not dissociated (or to a much lesser extent) at this wavelength. Generally, the loss of CO2 has been shown to be facile in deprotonated carboxylic acids from a range of collision-induced dissociation and mass spectrometry studies.38–43 However, these studies only characterize ground-state CO2 loss. In contrast, our photoinitiated experiments show a wavelength-dependent CO2 loss, which is a typical signature of an excited-state process. Finally, it is worth noting that the direct photodetachment (plus prompt autodetachment)5,19 channel at hv = 4.66 eV is larger than that at hv = 4.13 eV, supporting different branching ratios between internal conversion and direct photodetachment (or prompt autodetach-
ment), which is consistent with two different resonances being excited at 4.13 and 4.66 eV.

Taking all data together, the consistent mechanistic interpretation is the two-step reaction summarized in Figure 4. First, photoexcitation of the \([\text{C}_7\text{H}_9-\text{CO}_2]^-\) resonance at \(\sim 4.2\) eV initiates charge transfer from the CO2 group to the polyyene chain. There is an associated weakening of the \(\text{C}_7\text{H}_9-\text{CO}_2\) bond, which probably induces loss of CO2 on an excited-state potential energy surface to form ground-state \([\text{C}_7\text{H}_9^-]^-\). Our calculations predict that this process would produce \([\text{C}_7\text{H}_9^-]^-\) with \(\sim 1.9\) eV of internal energy. A second photon in the same laser pulse can probe \([\text{C}_7\text{H}_9^-]^-\). In contrast, the \([\text{C}_7\text{H}_9-\text{CO}_2]^-\) resonance at \(\sim 4.5\) eV that is photoexcited at \(\hbar\nu = 4.66\) eV is much brighter and involves a \(\pi^* \leftarrow \pi\) transition but does not involve excitation character that would promote excited-state dissociation of CO2. Hence, \([\text{C}_7\text{H}_9^-]^-\) is not formed directly from the 4.5 eV resonance, and thermoionic emission occurs solely from the parent ground state. In the second mechanistic step, the vibrationally hot but ground electronic state \([\text{C}_7\text{H}_9]^-\) produced after 4.13 eV excitation can undergo an intramolecular rearrangement to ultimately dissociate \(\text{H}^-\). We propose that the most likely mechanism of such a rearrangement will involve a cyclization reaction to form toluene + \(\text{H}^-\) due to the high stability of toluene. Such a cyclization would require a series of trans to cis isomerizations about the double bonds, the first of which may be initiated on the excited-state surface or thermally on the ground state. Isomerization transition state barriers in polyene chains are typically 0.3–1.3 eV in the ground electronic state or can be much smaller in excited electronic states, implying that several trans–cis isomerizations would be available with the thermal energy of \([\text{C}_7\text{H}_9^-]^-\). We calculate the asymptotic \(\Delta E\) for the cyclization reaction to be \(-0.40\) eV (\(-39\) kJ mol\(^{-1}\)), that is, exothermic, supporting that the cyclization reaction is thermally accessible (assuming that the transition state barrier is less than the total vibrational energy). However, we note that a second photon could also be absorbed by \([\text{C}_7\text{H}_9^-]^-\) to photochemically promote cyclization. Experimental studies on similar conjugated molecules and polyenes have shown that gas-phase intramolecular cyclization reactions can commonly yield toluene, although it is noteworthy that the present system represents one of the smallest polyenes to yield toluene. Unfortunately, because toluene is neutral, it is difficult to use conventional mass spectrometry methods for characterization, although ion mobility spectrometry may prove useful to characterize the \([\text{C}_7\text{H}_9^-]^-\) intermediate species and its isomer distribution.

In summary, we have shown that a rich interplay of dynamics can occur in the detachment continuum of large aromatic anions. The present study has extended the current understanding to demonstrate that the dynamics of resonances can induce specific dissociation processes and therefore facilitate wavelength-specific photochemistry. In \([\text{C}_7\text{H}_9-\text{CO}_2]^-\), specific resonance dynamics induce rapid depcarboxylation, which subsequently leads to an intramolecular reaction of the \([\text{C}_7\text{H}_9^-]^-\) product. Our work provides the first evidence of a photoinduced cyclization reaction in an anionic polyyene and highlights the utility of photoelectron and fragment imaging to probe photochemical reaction intermediates and final products.

**METHODOLOGY**

The experimental setup has been described in detail elsewhere, and only a brief overview with details specific to the present work follows. The gaseous ion \([\text{C}_7\text{H}_9-\text{CO}_2]^-\) (Figure 1) was generated by electrospray ionization of \(\sim 1\) mM solutions of \([\text{C}_7\text{H}_9-\text{CO}_2\text{H}]\) (Sigma-Aldrich) dissolved in methanol with a small amount of ammonia to aid deprotonation. Gaseous ions entered a vacuum system through a capillary and were guided into a ring-electrode ion trap. The trapped ions were thermalized and injected into a Wiley-Maclaren time-of-flight mass spectrometer with a 10 Hz repetition rate. The focus of the mass spectrometer coincided with the center of a perpendicular VMI spectrometer. Mass-selected ion packets were intersected with laser pulses (~5 ns duration) from a Nd:YAG pumped OPO operating at 4.13 eV (300 nm) or 4.66 eV (266 nm). The VMI spectrometer is usually operated as a photoelectron spectrometer, where the photoelectrons impact on a gated (100 ns) MCP detector coupled to a phosphor screen. The resulting events are digitally captured using a CCD camera. For photoelectron spectroscopy, the parent ion beam energy has only a small influence on the electron trajectories because of the very large mass difference between the parent ion and photoelectrons. VMI images were reconstructed using the polar-onion peeling algorithm, and photoelectron spectra were calibrated using the photoelectron spectrum of \(\text{I}^-\). The resolution of the photoelectron spectra is ~5%.

Supporting electronic structure calculations were performed with Gaussian 09 and GAMESS-US. First, CAM-B3LYP//aug-cc-pVTZ calculations were performed to determine equilibrium geometries, and G4 theory was used to compute thermochemical properties. Calculation of resonance energies for \([\text{C}_7\text{H}_9-\text{CO}_2]^-\) was performed at the multistate XCMQDPT2 level of theory using the aug-cc-pVQZ basis set excluding the most diffuse set of d functions on carbon atoms for computational tractability. The CASSCF reference wave function used 10 electrons in 13 orbitals, which constituted the most important p, \(\pi\), and \(\pi^*\) orbitals from a preliminary CIS calculation. This level of theory has previously proven reliable to determine resonance energetics in a range of conjugated and aromatic anions.
REFERENCES


