Communications to the Editor

Experimental and Computational Studies of the Structures and Energetics of Cyclooctatetraene and Its Derivatives

Shuji Kato, Hack Sung Lee, Roustam Gareyev, Paul G. Wenthold,[†] W. Carl Lineberger,*[,†] Charles H. DePuy,* and Veronica M. Bierbaum*

Department of Chemistry and Biochemistry
JILA, University of Colorado and National Institute of Standards and Technology
University of Colorado, Boulder, Colorado 80309

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Conformational changes in cyclooctatetraene (COT) and its substituted derivatives have been the subject of considerable interest for several decades.[1,2] Relatively little is known, however, about the thermochemical properties of COT and, in particular, its radical and anionic derivatives. We have employed the selected-ion flow tube (SIFT) technique, photoelectron spectroscopy (PES), and molecular orbital (MO) calculations for a comprehensive study of the structures and energetics of C_8H_n and $C_8H_n^-$ ($n = 6-8$). We report the electron affinities, gas-phase acidities, and C−H bond dissociation energies for COT and the related radicals. In addition, we have observed unusual properties for the electronic structure and reactivity of the $C_8H_7^-$ anion, which is shown to have a novel π-electron configuration and which exhibits a rare example of collision-induced *isomerization* leading to transannular bond formation.

Electron affinities (EA) were determined from SIFT and PES measurements. The EA of COT was obtained from the forward and reverse reaction rate constants for the electron-transfer equilibrium (eq 1). The rate constants were measured separately

$$\mathrm{COT} + \mathrm{O_2}^- \underset{k_r}{\overset{k_f}{\rightleftharpoons}} \mathrm{COT}^- + \mathrm{O_2} \qquad (1)$$

at 300 K in the SIFT, with $k_f = 8.70(\pm 0.70) \times 10^{-10}$ and $k_r = 1.97(\pm 0.20) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}. The free energy change ΔG_{Rxn} is derived from the equilibrium constant K_{eq} ($\equiv k_f/k_r$) as −2.26 kcal/mol. The entropy change ΔS_{Rxn} is small (0.21 cal/(mol K)),[3] and the reaction enthalpy ΔH_{Rxn} is estimated as −2.20 kcal/mol. Using the well-established EA for O_2 (0.451 ± 0.007 eV),[5] the EA for COT is determined as 0.55 ± 0.02 eV (Table 1). This value is supported by separate experiments in which COT^- or O_2^- ions were injected into the flow tube containing known COT/O_2 mixtures and the equilibrium constant was directly measured. The equilibrium measurement also insures that the measured EA reflects the adiabatic transition between COT and COT^-.

Table 1. Thermochemical Data for COT and Its Derivatives

RH	ΔH_{acid} (kcal/mol)	EA (eV)	BDE (R−H)[a] (kcal/mol)
C_8H_{10}			82.6 ± 3.8
C_8H_9	349.9 ± 4.1		49.1 ± 4.1
C_8H_8	381.3 ± 2.3	0.55 ± 0.02	93.0 ± 2.3
C_8H_7	357.2 ± 8.3	1.091 ± 0.008	67.8 ± 8.3
C_8H_6		1.044 ± 0.008[b]	

[a] Calculated using eq 2 or 3. [b] Reference 11.

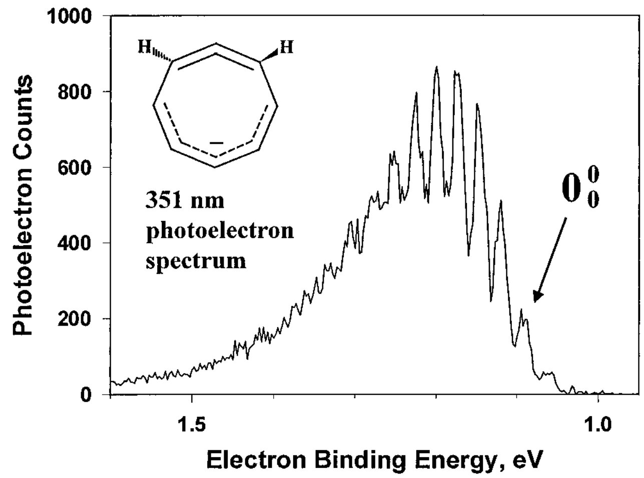

Figure 1. The 351 nm photoelectron spectrum of $C_8H_7^-$ in the range of 1.6−1.0 eV. The origin peak is assigned on the basis of the temperature dependence. The structure of $C_8H_7^-$ is deduced from molecular orbital calculations and angular distribution measurements (see text).

The *adiabatic* EA of COT has been controversial for many years, and values of 0.58 ± 0.04 eV (thermal electron attachment),[6] <0.8 eV (photodetachment),[7] and ∼0.65 eV (PES combined with an experimental estimate of the COT ring inversion barrier)[8] have been reported. The EA for this species is difficult to determine since the transition between the ground states of COT (tub-like)[1,2] and COT^- (planar)[9] involves a very large conformational change. From the difference between the electron binding energy of the transition state for COT ring inversion (1.099 eV)[8] and the adiabatic EA, the barrier for ring inversion is calculated to be 12.7 ± 0.5 kcal/mol; this value is similar to or slightly higher than those inferred from previous experiments[10] but is considerably smaller than those for highly substituted derivatives of COT.[2b,c]

The EAs of C_8H_6 and C_8H_7 were obtained using PES of $C_8H_6^-$ and $C_8H_7^-$ (Table 1). The photoelectron spectrum of $C_8H_6^-$ is very similar to that of COT^-. The ground state of the neutral C_8H_6 formed upon electron-detachment of the ion

[†] JILA.

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(3) The value for ΔS_{Rxn} is estimated from calculated entropies for COT and COT^- using the CBS-4 procedure (ref 4) which is included in *Gaussian 94* and those for O_2 and O_2^- using a statistical treatment. On the basis of HF/3-21G* calculations, COT loses low-frequency bending (201.8 cm^{-1}) and torsion (264.0 cm^{-1}) modes upon electron attachment to form COT^-, which in turn acquires low-frequency out-of-plane bending modes at 107.0 and 237.3 cm^{-1}. Taking into account all of the vibrational modes involved, the increase in vibrational entropy is 0.41 cal/(mol K) in going from COT to COT^-. The overall ΔS_{Rxn} is obtained after correction for the rotational entropies for COT and COT^- and the vibrational/rotational entropies for O_2 and O_2^-.
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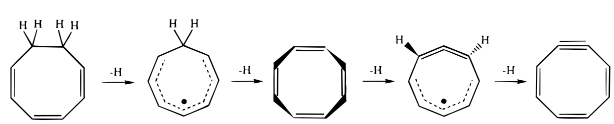
has an EA of 1.044 eV and is calculated to have a planar or pseudoplanar cyclooctatrienyne structure.[11]

The photoelectron spectrum of $C_8H_7^-$ (Figure 1) is significantly different from that of $C_8H_6^-$ (ref 11) or $C_8H_8^-$ (ref 8). Unlike that for those ions, the feature corresponding to the ground state consists of an extended 220 cm^{-1} vibrational progression. The origin was identified by varying the temperature of the ion source, giving an $EA(C_8H_7) = 1.091 \pm 0.008$ eV. The measured electron binding energies of $C_8H_6^-$ and $C_8H_7^-$ are consistent with observations that both ions undergo rapid electron transfer to SO_2 (EA = 1.107 eV).[12]

We have used MO calculations to investigate the structures of $C_8H_7^-$ and C_8H_7. At the R(O)HF/6-31G* level of theory, two distinct structures are found for both $C_8H_7^-$ and C_8H_7: a tub-like species that is similar to COT, except missing a proton/hydrogen and a C_2 species that is best described as a cyclic allene containing a pentadienyl moiety. At the Becke3LYP/6-311G(2df,p) level of theory, the C_2 form is lower in energy than the tub-like form by ~7 kcal/mol in both the ion and the radical, suggesting that the ground states of $C_8H_7^-$ and C_8H_7 are delocalized π-systems. This assignment is consistent with the measured anisotropy parameter for detachment of $C_8H_7^-$, $\beta = -0.55$. This value is similar to those obtained for detachment of π-anions, such as allyl[13] and benzyl[14] anions, and is much different from values expected for detachment from a vinylic orbital such as in phenyl anion[14] where $\beta > 0$. The 220 cm^{-1} vibration observed in the spectrum is assigned on the basis of R(O)HF calculations to a torsional mode of the cyclic allene in which the allenic moiety approaches a geometry closer to planarity.

The acidities (ΔH_{acid}) of C_8H_9, C_8H_8, and C_8H_7 were bracketed by proton-transfer reactions of $C_8H_8^-$, $C_8H_7^-$, and $C_8H_6^-$, respectively (Table 1). The acidity of C_8H_9 lies between that of CH_3COOH (ΔH_{acid} = 348.7 kcal/mol) and H_2S (351.1 kcal/mol). The value of ΔH_{acid} (C_8H_7) is greater than ΔH_{acid} [$(CH_3)_3CSH$] (352.5 kcal/mol), while extensive H/D exchange between $C_8H_6^-$ and CF_3CH_2OD[15] shows that ΔH_{acid} (C_8H_7) is lower than ΔH_{acid} (CF_3CH_2OH) (361.9 kcal/mol). The acidity of C_8H_8 lies between CH_3OH (380.5 kcal/mol) and H_2O (390.8 kcal/mol)[16] and is closer to the former. Rate constants were measured for the proton-transfer equilibrium $C_8H_7^- + CH_3OH \rightleftharpoons C_8H_8 + CH_3O^-$ [$k_f = 1.0(\pm 0.1) \times 10^{-9}$ and $k_r = 2.6(\pm 0.3) \times 10^{-10}$ cm^3 $molecule^{-1}$ s^{-1}]. Assuming $\Delta\Delta S_{acid} \cong 0$, ΔH_{acid} (C_8H_8) was derived from the equilibrium constant to be 381.3 kcal/mol. This value is much larger than that for C_8H_7 or C_8H_9, but smaller than that expected for a vinylic system, a difference readily understood if the negative ion formed upon deprotonation of COT is a delocalized π-system rather than a localized vinylic anion.

These results allow us to calculate the sequential bond energies (Table 1) for the processes shown below. The C−H



1 2 3 4 5

bond dissociation energies (BDE) for C_8H_9, C_8H_8, and C_8H_7 are obtained from the EA and ΔH_{acid} using the relation:

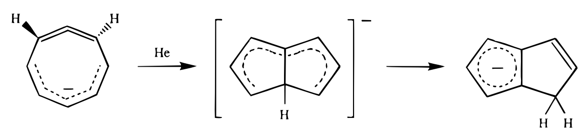
$$\mathrm{BDE\ (R-H)} = \Delta H_{acid}\,(\mathrm{RH}) + \mathrm{EA\ (R)} - \mathrm{IP\ (H)} \quad (2)$$

In addition, the C−H bond energy in C_8H_{10} [BDE(C_8H_{10})] can be determined using eq 3.

$$\mathrm{BDE\ }(C_8H_{10}) = \Delta H_f\,(C_8H_8) - \Delta H_f\,(C_8H_{10}) - \mathrm{BDE\ }(C_8H_9) + \mathrm{BDE\ }(H_2) \quad (3)$$

The C−H bond strength in COT (93.0 kcal/mol) is significantly weaker than C−H bonds of typical sp^2 carbons [BDE (ethylene) = 111.2 kcal/mol[17] and BDE (benzene) = 113.5 kcal/mol[18]], but is similar to those for propene (88.8 kcal/mol) and toluene (89.8 kcal/mol).[19] This supports structure **4**, where C_8H_7 acquires additional stabilization by delocalizing the radical electron within the ring.

If the SIFT injection energy is increased, we observe a significant change in the reactivity of the $C_8H_7^-$ ion. For example, after injection at 50 eV the $C_8H_7^-$ ion is unreactive with CH_3OH. This suggests that the $C_8H_7^-$ ion (**6**) undergoes isomerization upon injection into the flow tube and collision with helium, the extent of isomerization depending on the SIFT injection energy. A bicyclic [3.3.0] structure (**7**) is deduced from its chemical reactivity and MO calculations.[15] Although

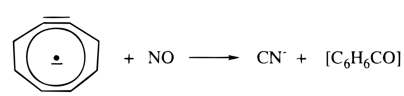


(4)

6 **7**

collision-induced dissociation is ubiquitous, examples of collision-induced isomerization of negative ions are relatively rare[20] and are difficult to detect by most experimental techniques. Duplication of this novel isomerization in solution would provide convenient entry into bicyclic ring systems which pose significant synthetic challenges.

The $C_8H_n^-$ ions exhibit intriguing chemistry. For example, the $C_8H_6^-$ ion (**8**) undergoes a remarkable, fairly rapid reaction with NO to form CN^- and, presumably, either tropone or benzene and carbon monoxide as neutral products. The



(5)

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reactions of these ions will be fully discussed in a future publication.[15]

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