

Reactivity and Thermochemistry of Quadricyclane in the Gas Phase

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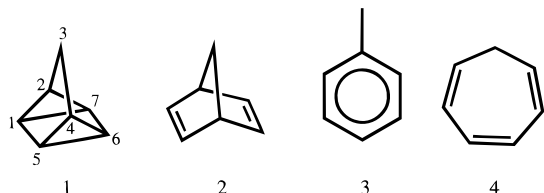
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Abstract: The gas-phase acidity of quadricyclane, C_7H_8 , has been determined using a flowing afterglow-selected ion flow tube at room temperature. Measurements of forward and reverse rate constants for the proton transfer reactions $B^- + C_7H_8 \rightleftharpoons C_7H_7^- + BH$ where $BH = NH_3$, CH_3NH_2 , and C_6H_6 give $\Delta_{acid}G_{300}(C_7H_8) = 394.7 \pm 0.8$ kcal/mol and $\Delta_{acid}H_{300}(C_7H_8) = 403.0 \pm 1.1$ kcal/mol. Combining this value with the electron affinity, 0.868 ± 0.006 eV, of the quadricyclyl radical, gives 109.4 ± 1.3 kcal/mol for the C–H bond dissociation energy of quadricyclane at C1. Reactions of quadricyclanide ion with various reagents have been studied, and branching ratios of product channels have been determined. These results, along with *ab initio* calculations and a companion photoelectron spectroscopy study, indicate that there are two isomers of quadricyclanide ion which have similar energies.

Introduction

Quadricyclane (tetracyclo[3.2.0.0.2⁷.0.4⁶]heptane) is a highly strained member (1) of the C_7H_8 family of hydrocarbon compounds which include norbornadiene (2), toluene (3), and cycloheptatriene (4) among others. The strain energy of



quadricyclane is evident in a comparison of the heats of formation of these compounds which are 80 ± 1 , 57.0 ± 1.0 , 12.0 ± 0.1 , and 43.7 ± 0.2 kcal/mol, respectively.^{1,2} Quadricyclane is formed by rapid ring-closure of norbornadiene when irradiated by ultraviolet light; it is relatively stable at room temperature but reverts to norbornadiene when heated to 140° .^{3,4} Due to these properties, quadricyclane has been investigated as a candidate for solar-to-thermal energy conversion systems.^{5,6} Quadricyclane radical cation has been studied by time-resolved EPR spectroscopy in solution⁷ and by low-temperature EPR spectroscopy in matrices.^{8,9} The temperature and pressure

dependence of the vibrational spectra and the phase transition of quadricyclane in the solid phase have also been studied.¹⁰ The accompanying paper (*J. Am. Chem. Soc.* **1996**, *118*, 5074)¹¹ provides a good summary of recent literature on several isomers of C_7H_8 and C_7H_7 .

In contrast to norbornadiene, toluene, and cycloheptatriene, very little is known about the gas-phase chemistry and thermochemistry of quadricyclane and its anion. In this paper, we report the gas-phase acidity of quadricyclane, and by use of the electron affinity of the quadricyclyl radical reported in the accompanying paper (*J. Am. Chem. Soc.* **1996**, *118*, 5074)¹¹ we have determined the C–H bond dissociation energy. These values are of interest because there is little information available on the effect of strain on C–H bond dissociation energies, and quadricyclane is a highly strained molecule. We have also studied the reactivity of quadricyclanide ion with various reagents, including CS_2 , COS , CO_2 , N_2O , CH_3Cl , and $(C_2H_5)_2O$. We have carried out *ab initio* calculations to assess the relative stability of two quadricyclanide ion structures, their electron binding energies and their entropies of acidity. These studies provide a comprehensive overview of the chemistry and thermochemistry of quadricyclane in the gas phase.

Experimental Section

Reactions were studied at room temperature with our tandem flowing afterglow-selected ion flow tube (FA-SIFT), which has been described in detail elsewhere.¹² Negative ions are created by electron impact ionization and ion–molecule reactions in the source flow tube at helium pressures of 0.2 Torr. Ions are selected by a quadrupole mass filter and injected into the reaction flow tube at 0.5 Torr helium pressure. The gases and liquids used in this experiment are as follows: quadricyclane (Aldrich, 99%), ammonia (Matheson, Anhydrous 99.99%), monomethylamine (Matheson, 99.5%), benzene (J. T. Baker, 99.9%), and ammonia- d_3 (Cambridge Isotope Laboratories, 99% d). Proton NMR spectra of the quadricyclane sample indicates that there is a minor

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Table 1. Rate Constants, Equilibrium Constants and Gas-Phase Acidity Values for Quadricyclane Relative to Three Bases at 300 K
$$B^- + C_7H_8 \xrightleftharpoons[k_r]{k_f} C_7H_7^- + BH$$

BH	$\Delta_{\text{acid}}G(\text{BH})$ (kcal/mol)	k (cm ³ /s)	K_{eq}	$\Delta_{\text{acid}}G(C_7H_8)$ (kcal/mol)
NH ₃	396.4 ± 0.4 ^a	$k_f = 8.1 \pm 0.2$ (−10) ^b $k_r = 8.0 \pm 1.0$ (−11)	10.1 ± 1.3	395.0 ± 0.5
CH ₃ NH ₂	395.8 ± 0.5 ^c	$k_f = 7.2 \pm 0.8$ (−10) $k_r = 9.7 \pm 0.6$ (−11)	7.4 ± 0.9	394.6 ± 0.6
C ₆ H ₆	392.9 ± 0.4 ^d	$k_f = 2.2 \pm 0.8$ (−12) $k_r = 3.2 \pm 0.4$ (−11)	0.067 ± 0.027	394.5 ± 0.6

^a References 28 and 29. ^b 8.1 (−10) represents 8.1×10^{-10} . ^c This work. ^d Reference 14.

norbornadiene impurity (<1%) but no detectable toluene impurity (<0.1%). Amide ions, NH₂[−], are created in the source by electron impact on ammonia, then mass selected by a quadrupole mass filter and allowed to react with quadricyclane in the reaction flow tube. For the reverse reaction, quadricyclanide ion is created in the source by reaction of amide ion and quadricyclane and then mass selected and injected into the reaction flow tube and allowed to react with ammonia. Care must be taken in the creation of quadricyclanide ion in the source, since isomers of lower energy might be formed, as indicated by the slight upward curvature in the plot of logarithm of the signal *vs* the reaction distance. The effect of more slowly reacting isomers can be minimized, and accurate reaction rate coefficients can be obtained by kinetic analysis at early reaction times and small reagent flow rates.

The acidity of quadricyclane was also measured relative to monomethylamine and benzene. We have re-examined the gas-phase acidity of monomethylamine with our SIFT instrument; this value was previously determined in flowing afterglow studies.¹³ We have measured the proton transfer rate coefficients for the forward reaction of amide ion with monomethylamine and reverse reaction of monomethylamide ion with ammonia. Amide ion was created as described above, and CH₃NH[−] ion was created in the source by the reaction of amide ion with monomethylamine (direct electron impact on CH₃NH₂ was not very efficient in producing CH₃NH[−]). The measured rate coefficients are $k_f = 1.1 (\pm 0.1) \times 10^{-9}$ cm³/s and $k_r = 4.0 (\pm 0.3) \times 10^{-10}$ cm³/s, resulting in $K_{\text{eq}} = 2.8 \pm 0.3$ and $\Delta_{\text{rxn}}G = -0.6 \pm 0.1$ kcal/mol. For the reactions with quadricyclane, the same method was used to create CH₃NH[−] ion in the source.

Since the gas-phase acidity of benzene was re-measured recently,¹⁴ we employ this value in our study. For the reactions with quadricyclane, phenide ion, C₆H₅[−], was created in the source from reaction of amide ion with benzene. For all the reactions studied, small amounts of HO[−] ion were formed in the downstream flow tube by reaction with water impurity, since the quadricyclanide ion and NH₂[−], CH₃NH[−], and C₆H₅[−] ions are more basic than hydroxide ion.

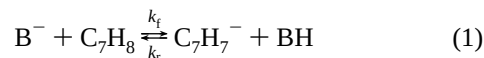
When hydroxide ion, HO[−], is used as a precursor to create C₇H₇[−] ion in the source, quite different reactivity was observed. With this mode of preparation, C₇H₇[−] ion is primarily benzyl anion, as confirmed by studies of its chemical reactivity and by parallel photoelectron studies.¹¹ For example, the reaction rate with water is 3 orders of magnitude slower than the collision rate. Reaction of this ion with D₂O results in only 2 H/D exchanges, confirming that this ion is indeed benzyl anion. The benzyl anion is presumably formed in the source by an extremely slow proton transfer–isomerization reaction via a long-lived collision complex: HO[−] + (1) → C₆H₅CH₂[−] + H₂O. This reaction is exothermic by 78 kcal/mol. Collision induced dissociation (CID) studies of quadricyclanide, norbornadienide, and benzyl anion were carried out by raising the SIFT injector plate to 75 V relative to the ion source. CID of the quadricyclanide ion, generated from the reaction of amide and quadricyclane, forms acetylide ion (74%) as the major product, with smaller amounts of C₅H₅[−] (18%) and C₃H₃[−] (8%). CID of the norbornadienide ion was distinctly different, forming acetylide ion (98%) almost exclusively with only a trace of C₅H₅[−] (2%); there was no evidence for production of C₃H₃[−]. Injection of the benzyl anion under these conditions did not produce fragment ions. These

experiments demonstrate that quadricyclanide ion retains its structure in the source and does not readily isomerize to norbornadienide anion or benzyl anion.

The number of acidic sites in quadricyclane was probed by H/D exchange reactions with ND₃. Electron transfer reactions of quadricyclanide ion with SO₂, CS₂, and O₂ were studied to estimate the electron affinity (EA) of the C₇H₇ radical. Reactions with CS₂, COS, CO₂, and N₂O were examined and found to give numerous products including adducts. Nucleophilic substitution (S_N2) reactions with CH₃Cl and elimination (E2) reactions with (C₂H₅)₂O were also studied and rate coefficients were measured.

Results and Discussion

The gas-phase acidity of quadricyclane has been obtained from the equilibrium constant, K_{eq} , by measuring forward (k_f) and reverse (k_r) reaction rate coefficients with compounds of known acidity (eq 1), i.e., $K_{\text{eq}} = k_f/k_r$.

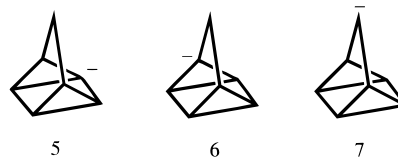


The values for the acidity of quadricyclane, $\Delta_{\text{acid}}G$, along with forward/reverse reaction rate coefficients determined using three bases are shown in Table 1. Note that the acidities of monomethylamine and benzene were determined using ammonia as an anchor base. From the known $\Delta_{\text{acid}}G$ (B) of these three bases, $\Delta_{\text{acid}}G$ (QC) of quadricyclane can be determined (eq 2).

$$\Delta_{\text{acid}}G(\text{QC}) = \Delta_{\text{acid}}G(\text{B}) - RT \ln K_{\text{eq}} \quad (2)$$

The three values of $\Delta_{\text{acid}}G$ fall within experimental uncertainties; an average value $\Delta_{\text{acid}}G = 394.7 \pm 0.8$ kcal/mol is reported.

We have studied H/D exchange reactions of quadricyclanide ion with ND₃ to determine the number of acidic sites in quadricyclane. Up to five H/D exchanges were readily observed. These results suggest that there are six acidic sites and that the four equivalent hydrogens at the four-membered ring [sites C1, C5, C6, and C7 in 1], and the two equivalent hydrogens at the three-membered rings [sites C2 and C4 in 1] have similar acidities. Thus, structures 5 and 6 are predicted to have similar stability; there is no evidence for the formation of structure 7. An alternative explanation for the H/D exchange results is that the anion rapidly rearranges to scramble the 1- and 2-positions. However, skeletal rearrangements of anions are not common.

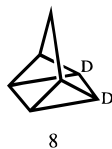


The existence of six sites in quadricyclane of similar acidity is corroborated by our studies of the reaction of amide ion with

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dideuterated quadricyclane (**8**). This reaction proceeds by 63%/



37% loss of H^+/D^+ ; these values are close to the statistical ratios (67%/33% loss of H^+/D^+) in a system containing four hydrogens and two deuteriums of comparable acidity. It should be mentioned that, for norbornadienide ion reacting with ND_3 , three H/D exchanges have been observed.¹⁵

To estimate the entropy of acidity, we employed *ab initio* calculations. The geometries and energies of quadricyclane (**1**) and quadricyclanide ion (**5**, **6**) were calculated using Gaussian-92¹⁶ with MP3 (frozen core)/6-31++G**//RHF/6-31++G** basis sets. The rotational constants and vibrational frequencies (uncorrected) were used to calculate the entropy change of deprotonation. The entropies of **1**, **5**, and **6** are 67.9, 69.4, and 69.3 cal/mol K, respectively, at 300 K (Table 2). Using the entropy of the proton, 26.0 cal/mol K, we obtain $\Delta_{acid}S$ (**5**) = 27.5 cal/mol K and $\Delta_{acid}S$ (**6**) = 27.4 cal/mol K (eq 3).

$$\Delta_{acid}S = S(C_7H_7^-) + S(H^+) - S(C_7H_8) \quad (3)$$

The enthalpy change at 300 K was then obtained using eq 4.

$$\Delta_{acid}H = \Delta_{acid}G + T\Delta_{acid}S \quad (4)$$

The acidity at 0 K ($\Delta_{acid}H_0$) was calculated using eq 5.

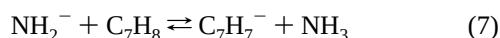
$$\Delta_{acid}H_0 = \Delta_{acid}H_T - \int_0^T \{C_p(C_7H_7^-) + C_p(H^+) - C_p(C_7H_8)\} dT \quad (5)$$

where C_p is the heat capacity. The heat capacities can be expressed as a function of temperature using rotational constants and vibrational frequencies obtained from *ab initio* calculations.¹⁴ The integral term is 1.6 kcal/mol for the quadricyclanide ion **5**. The C–H bond dissociation energy (BDE) can be calculated using eq 6, once EA(A) is known

$$BDE(A-H) = \Delta_{acid}H(AH) - IP(H) + EA(A) \quad (6)$$

where IP is the ionization energy of hydrogen atom (313.6 kcal/mol).

To estimate the upper limit of the EA of the C_7H_7 radical, the energetics of several reactions were compared. When O^- ion (heat of formation $\Delta_f H = 25.8$ kcal/mol) reacts with quadricyclane, the $C_7H_6^-$ ion as well as HO^- ion ($\Delta_f H = -32.8$ kcal/mol) are formed. Exothermic formation of the hydroxide ion and quadricyclyl radical requires that $\Delta_f H(C_7H_7)$ be less than 138.6 kcal/mol (Table 4a). To estimate the heat of formation of $C_7H_7^-$ ion, consider the enthalpy change of reaction 7.



From the free energy change $\Delta_{rxn}G = -1.7$ kcal/mol and the entropy change $\Delta_{rxn}S = \Delta_{acid}S(C_7H_8) - \Delta_{acid}S(NH_3) = 27.5 -$

25.0 cal/mol K = 2.5 cal/mol K, we obtain $\Delta_{rxn}H = -0.9$ kcal/mol for reaction 7. $\Delta_f H(C_7H_7^-)$ is determined to be 117.0 kcal/mol using $\Delta_f H(NH_2^-) = 26.9$ kcal/mol and $\Delta_f H(NH_3) = -11.0$ kcal/mol. In these estimations, $\Delta_f H(C_7H_8)$ is assumed to be 80 kcal/mol; however, this value is not needed in determining the upper limit of the EA, since it cancels out in the calculation. Hence EA(C_7H_7) is less than 21.6 kcal/mol (0.937 eV). Another way to estimate the EA is from bracketing reactions (Table 4b); electron transfer from quadricyclanide ion to SO_2 (EA = 1.107 eV)^{17,18} is fast; however, no electron transfer was observed to O_2 (EA = 0.451 eV).¹⁹ These reactions indicate that the EA of quadricyclyl radical is greater than 0.451 eV and less than 1.107 eV. Electron transfer to CS_2 (EA = 0.51 eV)²⁰ was not observed but the presence of other rapid reaction channels precludes any firm conclusions from this system. These estimates were helpful in the analysis of spectra in a concurrent photoelectron spectroscopy (PES) study. From the PES study,¹¹ two different EAs for quadricyclane are deduced, 0.868(6) and 0.962(6) eV. These two values probably correspond to two different isomers of structure **5** and **6**.

To estimate the relative energies of the quadricyclanide ions (**5**) and (**6**), we have performed *ab initio* calculations: MP3 (frozen core)/6-31++G** single point energy with fully optimized geometries and vibrational frequencies at the RHF/6-31++G** level (Table 2). The HF energy, MP3 energy, and zero point energy of quadricyclanide ion are -268.96181, -269.97073, and 0.12109 Hartrees for **5** and -268.96156, -269.97084, and 0.12074 Hartrees for **6**, respectively. The energy of **5** is greater than that of **6** by less than 0.3 kcal/mol including zero point energies; thus the stability of these two isomers is almost identical. The calculations show that structure **7** is a transition state.

For the electron affinities, calculations of the two quadricyclyl radical structures have been performed: MP3 (frozen core)/6-31++G** single point energy with fully optimized geometries and vibrational frequencies at the UHF/6-31++G** level. The HF energy, MP3 energy, and zero point energy of quadricyclyl radicals are -268.98626, -269.95620, and 0.12422 Hartrees for **5** and -268.98624, -269.95390, and 0.12412 Hartrees for **6**, respectively. The calculated electron binding energies (eBE) are eBE(**5**) = 0.40 eV, eBE(**6**) = 0.46 eV without zero point energies, and eBE(**5**) = 0.48 eV, eBE(**6**) = 0.54 eV with 90% zero point energy corrections. The 0.06 eV energy difference is almost entirely due to higher correlation energy of the quadricyclyl radical **5** compared to that of the radical **6**. These calculated eBEs are much lower than the experimental values. Another approach for evaluating eBEs is Koopmans' theorem which states that the electron binding energy of a closed-shell molecule is equal to the negative of the highest occupied orbital energy. Using this theorem, we obtain 1.61 and 1.74 eV for the eBEs of anions **5** and **6**, respectively. In this case, the eBEs are considerably higher than the experimental values, but the order is the same as from the previous estimation using the total energy. These estimates suggest that radical **6** has a higher EA than radical **5**.

Since sites C1 and C2 in quadricyclane have similar acidity, but the electron binding energies of the resulting anions **5** and **6** differ by almost 0.1 eV, the C–H bond dissociation energies at C1 and C2 must differ by this amount. Table 3 summarizes the acidities, $\Delta_{acid}G$, $\Delta_{acid}S$, and $\Delta_{acid}H$, and C–H bond

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Table 2. Parameters of Quadricyclane **1** and Quadricyclanide Ion **5** and **6** as Determined from *ab Initio* Calculations using Gaussian-92^b

	units	C ₇ H ₈ (1) (C _{2v})	C ₇ H ₇ [−] (5) (C ₁)	C ₇ H ₇ [−] (6) (C ₁)
HF energy	Hartrees	−269.63632	−268.96181	−268.96156
MP3 energy	Hartrees	−270.63748	−269.97073	−269.97084
zero point energy	Hartrees	0.13751	0.12109	0.12074
rotational constants	GHz	4.466, 4.407, 3.285	4.559, 4.517, 3.334	4.563, 4.463, 3.370
symmetry number		2	1	1
entropy	cal/mol K	67.9	69.4	69.3
vibrational frequencies ^a	cm ^{−1}	(A1) 797.2, 878.1, 983.3, 1037.6, 1095.0, 1197.3, 1414.1, 1502.1, 1621.4, 3188.2, 3340.0, 3377.6 (A2) 581.9, 805.8, 911.3, 1151.1, 1164.3, 1295.6, 1332.7, 3352.4 (B1) 423.9, 839.3, 969.0, 1000.0, 1130.7, 1196.5, 1403.8, 3226.8, 3363.7 (B2) 748.0, 777.2, 1018.5, 1077.7, 1131.0, 1367.1, 1427.7, 1529.3, 3336.9, 3365.3	412.6, 564.7, 690.3, 743.3, 768.2, 784.6, 809.2, 855.4, 888.7, 934.5, 973.5, 997.3, 1009.6, 1028.4, 1039.1, 1086.0, 1126.8, 1130.9, 1143.8, 1174.9, 1182.7, 1270.8, 1332.0, 1353.3, 1385.8, 1398.6, 1462.1, 1490.2, 1609.9, 3100.0, 3132.8, 3221.1, 3245.8, 3259.7, 3261.0, 3286.2	417.8, 574.3, 719.7, 756.5, 788.6, 790.2, 818.3, 851.6, 864.6, 936.5, 939.7, 994.6, 1003.0, 1005.7, 1055.0, 1067.4, 1088.4, 1126.6, 1145.7, 1156.3, 1231.4, 1267.6, 1302.9, 1320.6, 1350.6, 1361.2, 1388.4, 1493.8, 1599.6, 3113.5, 3131.8, 3244.3, 3250.5, 3262.5, 3278.9, 3299.3

^a The vibrational frequencies are not corrected. ^b Geometry and vibrational frequencies (RHF/6-31++G**), single point energy (MP3/6-31++G**).

Table 3. Gas-Phase Acidities and Bond Dissociation Energies (BDE) of Some C₇H₈ Isomers and Electron Affinities (EA) of the Corresponding C₇H₇ Radicals, at 300 K

C ₇ H ₈ isomers	Δ _{acid} G (kcal/mol)	Δ _{acid} S (cal/mol K)	Δ _{acid} H (kcal/mol)	EA(C ₇ H ₇) (eV)	BDE(C–H) (kcal/mol)
quadricyclane (5)	394.7 ± 0.8 ^a	27.5 ± 0.1 ^a	403.0 ± 1.1 ^{a,b}	0.868 ± 0.006 ^c	109.4 ± 1.3 ^{a,d}
(6)		27.4 ± 0.1 ^a	402.9 ± 1.1 ^a	0.962 ± 0.006 ^c	111.5 ± 1.3 ^{a,d}
norbornadiene	391.3 ± 1.5 ^e	27.4 ± 3.0 ^g	399.5 ± 1.7 ^g	1.286 ± 0.006 ^c	115.6 ± 1.9 ^a
toluene	373.7 ± 2.0 ^g	23.8 ± 1.4 ^g	380.8 ± 2.1 ^g	0.912 ± 0.006 ^f	88.0 ± 1.0 ^g
cycloheptatriene	369.2 ± 2.0 ^g	20.1 ± 2.6 ^g	375.2 ± 2.1 ^g	0.49 ± 0.13 ^g	73.0 ± 2.0 ^g

^a This work. ^b Δ_{acid}H(0 K) = 401.4 ± 1.1 kcal/mol calculated using eq 5. ^c The accompanying paper, ref 11 (J. Am. Chem. Soc. **1996**, *118*, 5074). ^d Two values of BDE(C–H) correspond to isomers of quadricyclyl radical corresponding to isomers of quadricyclanide ion (structures **5** and **6**). ^e Reference 15. ^f Reference 30. ^g References 2 and 31.

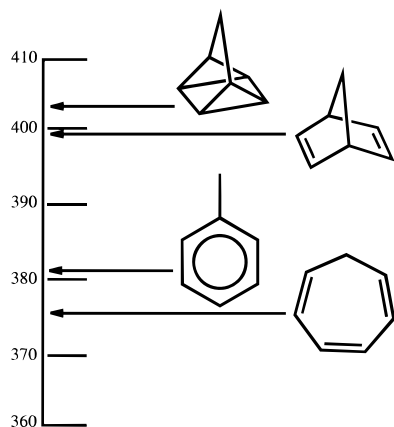


Figure 1. Gas-phase acidity scale of C₇H₈ isomers.

dissociation energies of some isomers of C₇H₈ (quadricyclane, norbornadiene, toluene, and cycloheptatriene), and the electron affinities of the corresponding radicals. Figure 1 shows the Δ_{acid}H₃₀₀ scale for these compounds. Both C–H bonds are extremely strong for saturated hydrocarbons, 109.4 ± 1.3 and 111.5 ± 1.3 kcal/mol for **5** and **6**, respectively, and are much more similar to those in ethylene (111.2 ± 0.8)²¹ than to those in cyclohexane (95.5 ± 1).²² However, the C–H bonds in cyclopropane have a BDE of 106.3 ± 0.3 kcal/mol,²² indicating that internal strain strengthens the bond. In general, alkyl radicals prefer to be planar or near-planar. The quadricyclyl

Table 4

a. Estimating the Upper Limit of the Electron Affinity of Quadricyclyl Radical (C ₇ H ₇) from Exothermic Reactions (Hydrogen Abstraction and Proton Transfer Reactions)		
O [−] + C ₇ H ₈ → HO [−] + C ₇ H ₇	ΔH _{rxn} ≤ 0	
NH ₂ [−] + C ₇ H ₈ → C ₇ H ₇ [−] + NH ₃	ΔH _{rxn} = −0.9 kcal/mol	
b. Bracketing of the Electron Affinity of Quadricyclyl Radical (C ₇ H ₇) from Electron Transfer Reactions		
C ₇ H ₇ [−] + SO ₂ → SO ₂ [−] + C ₇ H ₇	EA(SO ₂) = 1.107 eV	
C ₇ H ₇ [−] + CS ₂ → CS ₂ [−] + C ₇ H ₇	EA(CS ₂) = 0.51 eV	
C ₇ H ₇ [−] + O ₂ → O ₂ [−] + C ₇ H ₇	EA(O ₂) = 0.451 eV	

radicals formed by C–H bond dissociation will be far from planarity, and, presumably, this accounts for the strength of these bonds.

We examined the reactions of the mixture of quadricyclanide ions **5** and **6** with CS₂, COS, CO₂, and N₂O (Table 5).²³ In previous studies, we have shown that these reagents react in characteristic ways with carbanions of different structural types. For example, ions as strongly basic as **5** and **6** (e.g., the phenide ion, C₆H₅[−]) react with CS₂ almost exclusively by sulfur atom abstraction,²⁴ and indeed that is the predominant pathway (77%) observed. A host of other ions are formed in small amounts; we shall discuss their origin below.

Carbonyl sulfide (S=C=O) also transfers a sulfur atom in many of its gas-phase reactions with carbanions. This process is more exothermic than the corresponding reaction of CS₂, since the neutral product is CO rather than CS. It seems reasonable to propose that reactions of (**5**) and (**6**) with COS begin by sulfur

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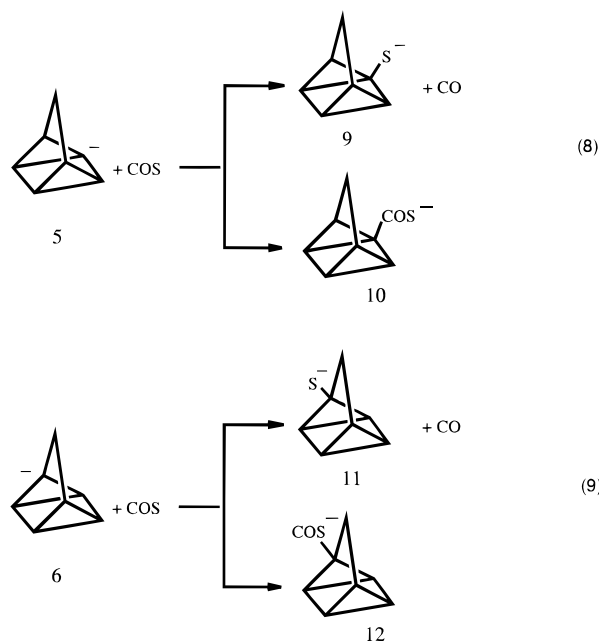
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Table 5. Branching Ratios of the Products of the Reactions of Quadricyclanide Ion with CS₂, COS, CO₂, and N₂O^a

$C_7H_7^- + CS_2 \xrightarrow{77\%} C_7H_7S^- + CS$		$C_7H_7^- + COS \xrightarrow{33\%} C_7H_7S^- + CO$	
$\xrightarrow{6\%} \text{adduct}$		$\xrightarrow{25\%} HC_2S^- + [C_5H_6 + CO]$	
$\xrightarrow{5\%} HS^- + [C_7H_6CS]$		$\xrightarrow{14\%} C_5H_5^- + HC_2COSH$	
$\xrightarrow{5\%} C_5H_5^- + HC_2CS_2H$		$\xrightarrow{12\%} HS^- + [C_7H_6CO]$	
$\xrightarrow{4\%} HC_2S^- + [C_5H_6CS]$		$\xrightarrow{6\%} HC_2COS^- + C_5H_6$	
$\xrightarrow{2\%} HC_2^- + [C_5H_5CS_2H]$		$\xrightarrow{6\%} \text{adduct}$	
$\xrightarrow{1\%} HC_2CS_2^- + C_5H_6$		$\xrightarrow{4\%} HC_2^- + [C_5H_5COSH]$	
$k(CS_2) = 7.4 \times 10^{-10} \text{ cm}^3/\text{s}$		$k(COS) = 5.2 \times 10^{-10} \text{ cm}^3/\text{s}$	
$C_7H_7^- + CO_2 \xrightarrow{35\%} C_5H_5^- + HC_2CO_2H$		$C_7H_7^- + N_2O \xrightarrow{26\%} HC_2O^- + [C_5H_6N_2]$	
$\xrightarrow{24\%} C_5H_5CO_2^- + C_2H_2$		$\xrightarrow{20\%} OH^- + [C_7H_6N_2]$	
$\xrightarrow{16\%} \text{adduct}$		$\xrightarrow{15\%} \text{adduct}$	
$\xrightarrow{15\%} HC_2CO_2^- + C_5H_6$		$\xrightarrow{12\%} HC_2N_2O^- + C_5H_6$	
$\xrightarrow{10\%} HC_2^- + [C_5H_5CO_2H]$		$\xrightarrow{10\%} C_7H_5^- + H_2O + N_2$	
		$\xrightarrow{7\%} C_5H_3O^- + [C_2H_4 + N_2]$	
		$\xrightarrow{5\%} C_5H_5^- + HC_2N_2OH$	
		$\xrightarrow{5\%} C_7H_7O^- + N_2$	

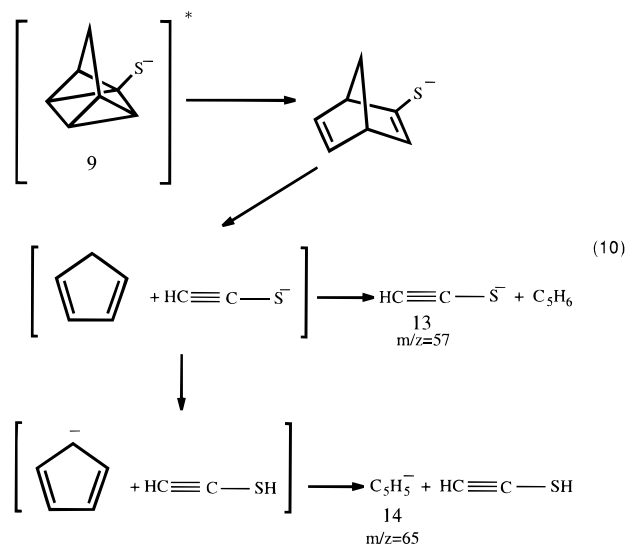
^a Total rate coefficients are shown for CS₂ and COS. Some neutral products, which may not be bound, are denoted by brackets. Experimental uncertainty for branching ratios of 10% or more is $\pm 5\%$.

abstraction, and, indeed, $C_7H_7S^-$ accounts for 33% of the product ions. Small amounts of adduct are also observed (eqs 8 and 9).



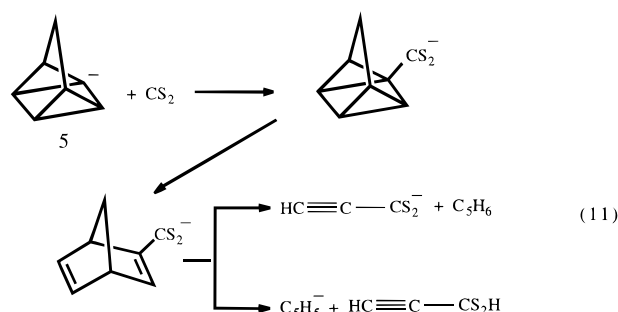
Because the reactions with COS are more exothermic than those with CS₂, the product ions will be generated with more internal energy, and they can undergo further reactions. For example, the ions of m/z 57 and m/z 65 (formulated as **13** and **14**, respectively) can arise naturally from **9** by reverse cycloaddition reactions (eq 10). A similar mechanism was invoked by MacMillan et al.²⁵ in the reactions of metal cations with quadricyclane.

The ion of m/z 85 can be written as $HC\equiv C-COS^-$, and can be formed analogously by fragmentation of the COS adduct ion **10**. Thus taken together, 45% of the product ions appear to arise by fragmentation of **9** and **10** while only 4% (HCC^- ,



m/z 25) are obviously formed by fragmentation of **11** and **12**, most of which probably remains undecomposed.

If we now return to the product ions from reaction with CS₂ we can see that these same ions are formed (with $HC_2CS_2^-$ replacing HC_2COS^-) (eq 11). Fragmentation of **(9)** again



exceeds that of **(11)**, although the total amount of fragmentation is reduced because of the lesser amount of internal energy in **(9)** and **(11)**.

This same pattern of reaction and fragmentation is also seen with CO₂, although with this reagent the initial step is addition

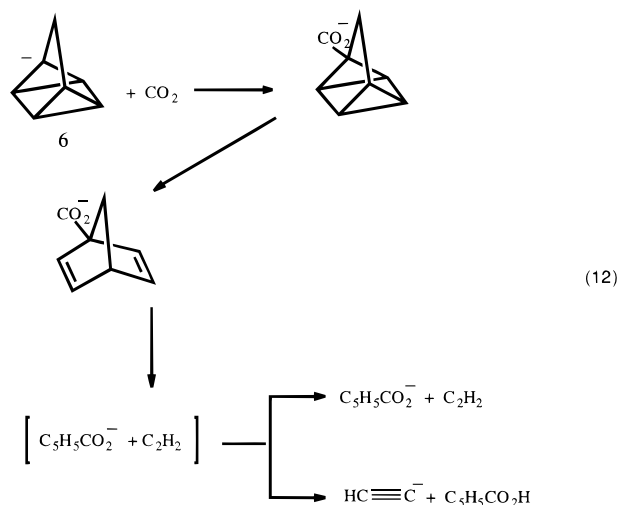
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Table 6. S_N2 and E2 Reactions of Quadricyclanide Ion with Methyl Chloride and Diethyl Ether^a

$C_7H_7^- + CH_3Cl$	$\xrightarrow{93\%} Cl^- + C_7H_7CH_3$	$k = 5.0 \times 10^{-10} \text{ cm}^3/\text{s}$
	$\xrightarrow{7\%} CH_2Cl^- + C_7H_8$	
$C_7H_7^- + (C_2H_5)_2O$	$\xrightarrow{\quad} C_2H_5O^- + C_2H_4 + C_7H_8$	$k \leq 1.2 \times 10^{-11} \text{ cm}^3/\text{s}$

^a Due to H₂O impurity in diethyl ether, only the upper limit is given.

rather than atom transfer. With no neutral product to carry away internal energy, the adduct fragments to a still greater degree, and we can see that 34% of the products must derive from the reaction of **6** (eq 12), while 50% of the products derive from reaction of **5**.



This same general pattern of addition or atom abstraction followed by ring-opening and fragmentation can be seen for the N₂O reactions, giving rise, for example, to HCCO⁻, HCCN₂O⁻, and C₅H₅⁻ from **5** and most likely C₅H₃O⁻ from **6**.

Thus the chemical reactions of the M - 1 ions from quadricyclane are consistent with the formation of a mixture of **5** and **6**, with **5** probably predominating.

Table 6 summarizes the reactions of quadricyclanide ion with methyl chloride and with diethyl ether.^{26,27} Reaction with methyl chloride proceeds rapidly with nucleophilic substitution

as the major pathway and proton abstraction as the minor channel. This reactivity pattern is expected for highly basic anions. The elimination reaction of quadricyclanide ion with diethyl ether is very slow; the endothermic proton abstraction which initiates this reaction is known to be slow for carbanions. This is in sharp contrast to the rapid elimination reactions that are often observed for basic anions of heteroatoms, such as HO⁻ and NH₂⁻.

Conclusions

The gas-phase acidity of quadricyclane has been measured to be Δ_{acid}G₃₀₀(C₇H₈) = 394.7 ± 0.8 kcal/mol and is the highest among the C₇H₈ isomers measured to date. H/D exchange reactions with ND₃ indicate that the hydrogen atoms at the three- and four-membered rings have similar acidity, giving rise to two isomeric quadricyclanide ions of similar stability. These conclusions are supported by reactions of C₇H₇⁻ with various reagents, by *ab initio* calculations and by examination of dideuterated quadricyclane. Bracketing of the electron affinity of quadricyclyl radical by electron transfer reactions proved helpful to parallel photoelectron spectroscopy experiments. Combination of the gas phase acidity of quadricyclane with the electron affinity of the quadricyclyl radical provides the C-H bond dissociation energy of quadricyclane.

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