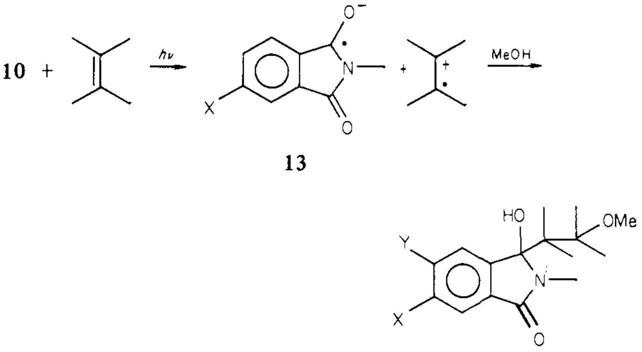
Table I. Product Distribution from Photolysis of 10

10	X = OMe	X = CH_3	X = Cl	X = CO_2Me
% 11	100	57	52	27
% 12	0	43	48	73
% yield (11 and 12)	32	32	45	46

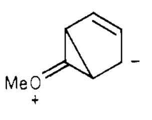
this reaction with a strong donor substituent (**10**, X = OCH_3) is **14a** (66:34 **14a**–**14b**), whereas with a strong acceptor (**10**, X = CO_2Me) the only product isolated is **15**.[16]



13

14a, X = H; Y = OCH_3
b, X = OCH_3; Y = H
15, X = CO_2Me; Y = H

In a concerted process, the product distribution should reflect the excited-state C–N double-bond character or excitation localization induced by the substituent. Although we have shown that the reaction proceeds via the singlet state,[17] we are unable to completely assess the nature of the reactive excited state at present. The application of excited-state criteria previously developed[19] predicts that donors direct incoming electrophiles meta in photochemical reactions. Incorporation of this model into the methoxyphthalimide system suggest that [2 + 2] addition of an alkene should occur at the position of maximum N–C double-bond character, i.e., bond a in **17**. Acceptor substituents should direct the incoming reactant to bond b. Irrespective of these arguments, we expect donor and acceptor substituents to have opposite effects, as they do in other photochemical reactions,[19] and result in different regiochemistry.



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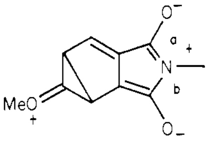
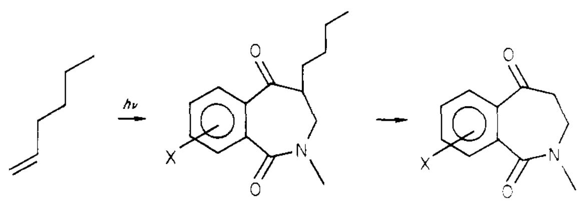
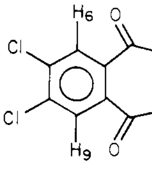


17

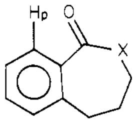
A series of substituted phthalimides **10** (X = OCH_3, CH_3, Cl, CO_2Me) were irradiated in the presence of 1-hexene in acetonitrile, and the products **19**, which result from a type II process on the initially formed products **18**,[1,9] were isolated. Structure proof for the two regioisomers **11** and **12** was provided by analysis of the aromatic region of the proton NMR spectrum of **20**, **21a**, and **21b**.[20] The spectrum of **20** shows the aromatic protons as singlets at δ 8.01 and 7.76 indicating that there are dramatic differences in the deshielding effects of the ketone and lactam moieties on the peri hydrogens. Our original assignment of the most downfield-shifted proton in **20** to H_6 was confirmed by examination of the spectrum of **21a** which showed the peri hydrogen (H_p) as a doublet of doublets at δ 7.72, whereas in **21b** this proton was part of the complex aromatic multiplet at δ 7.36–6.96.



18 19



20



21a, X = CH_2
b, X = NH

The structures of the photolysis products **11** and **12** follow from analysis of the coupling patterns of their most downfield-shifted protons. For example, the NMR spectrum of **11c** shows H_6 as a doublet (J = 8 Hz) at δ 7.88, whereas, for **12c** H_6 appears as a doublet (J = 2 Hz, meta coupling) at δ 7.88. Similar analysis gave the structures of the other **11**, **12** isomers.

The product distribution (Table I) is clearly inconsistent with the results of our radical anion trapping studies but in accord with our ad hoc prediction for a concerted reaction. Although we favor a concerted process for this reaction on the basis of these results and those of our stereochemical studies,[9] the possibility that the reaction might occur through an oriented exciplex which rapidly decays through a biradical (A ↔ B) to the product cannot be discounted completely.

Acknowledgment. We thank the National Science Foundation for their generous support.

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[17] Recent quenching studies on the intramolecular photoaddition of *N*-pentenylphthalimide, using 2,3-dimethyl-2-butene as an electron-transfer quencher, have resulted in the determination of a k_r for this reaction of ~10^8. Since the phosphorescence lifetime is ~1 s for *N*-propylphthalimide,[18] we conclude that the addition reaction proceeds via the singlet.[7]

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[20] Substituted phthalimides were synthesized by conventional methods. Isomeric benzazepinedione products were isolated by semipreparative HPLC on silica gel using ether–hexane as eluant. All new compounds gave acceptable IR, NMR, and analytical data. Details will be presented in a full paper on the subject.

Infrared Spectra of Gas-Phase Ions and Their Use in Elucidating Reaction Mechanisms. Identification of $C_7H_7^-$ Structural Isomers by Multiphoton Electron Detachment Using a Low-Power Infrared Laser

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The ability to distinguish structural isomers of ions on the basis of their vibrational spectra is of considerable interest since a general method would greatly extend the capabilities of mass spectrometry. It is difficult to achieve number densities of gas-phase ions sufficient to observe infrared absorption directly,[1-4] so indirect methods have been developed by inducing unimolecular[5] or modified bimolecular[6] reactivity as a result of absorption of one

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or more infrared photons. We have explored the technique of multiphoton dissociation using CW and pulsed infrared lasers to obtain spectra of positive ions.[7-10] Multiphoton electron detachment (MED) from negative ions was recently reported by Brauman and co-workers using high-power laser pulses from a CO_2-TEA laser.[11] These initial studies have inspired an interesting theoretical treatment of vibrationally induced electron detachment.[12] In this report we present the infrared MED spectra of isomeric $C_7H_7^-$ ions obtained with a low-power CW CO_2 laser. This methodology has been used to probe mechanistic details of an ion-molecule reaction in the gas phase for the first time, showing that deprotonation of 2,5-norbornadiene by CH_3O^- is accompanied by structural rearrangement to benzyl and cycloheptatrienyl anions.

The ion cyclotron resonance spectrometer and optical configuration have previously been described in detail.[13,14] Briefly, ions are trapped at low pressures, typically 10^{-6} torr, for periods up to several seconds during which they are irradiated with the unfocused output of a line tunable CW CO_2 laser (Apollo Lasers Model 550A). The anions of interest are formed by proton-transfer reactions of anionic bases[15] with the neutral C_7H_8 isomers in reactions 1-3.

$$CH_3O^- + C_6H_5CH_3 \rightarrow C_6H_5CH_2^- + CH_3OH \qquad (1)$$

$$CH_3O^- + c\text{-}C_7H_8 \rightarrow c\text{-}C_7H_7^- + CH_3OH \qquad (2)$$

$$NH_2^- + \text{norbornadiene} \rightarrow C_7H_7^- + NH_3 \qquad (3)$$

After an initial ion formation period, laser irradiation causes the ion population to decay exponentially in time with an induction period which is evident at laser intensities less than 20 W/cm^2.[14] Recycling of the detached electrons to form additional $C_7H_7^-$ is prevented by double-resonance ejection of the precursor base during the irradiation period.

The electron affinity of benzyl radical is 20 kcal/mol.[16] Therefore, a minimum of eight infrared photons must be absorbed by benzyl anion to reach the electron detachment threshold. Similarly, the electron affinity of cycloheptatrienyl radical is estimated to be 13 kcal/mol[17] so that at least five photons are required for direct electron detachment from the anion. Interestingly, the latter process might not occur directly if the barrier to isomerization from c-$C_7H_7^-$ to $C_6H_5CH_2^-$ is less than 13 kcal/mol. Following structural rearrangement, autodetachment of an electron would be expected because the heat of formation of cycloheptatrienyl anion is greater than that of benzyl radical and a free electron. Unfortunately, the two possible mechanisms may not be distinguished, since neutral products are not detected. Further details of the sequential multiple photon excitation process leading to electron detachment will be presented elsewhere.[18]

Infrared spectra of cycloheptatrienyl and benzyl anions are obtained by monitoring the extent of photodetachment as a function of laser wavelength at a fixed intensity and irradiation period (Figure 1a). Irradiation of $C_7H_7^-$ formed by deprotonation of norbornadiene with NH_2^- (reaction 3) results in no detectable electron detachment, indicating a third distinct $C_7H_7^-$ isomer.

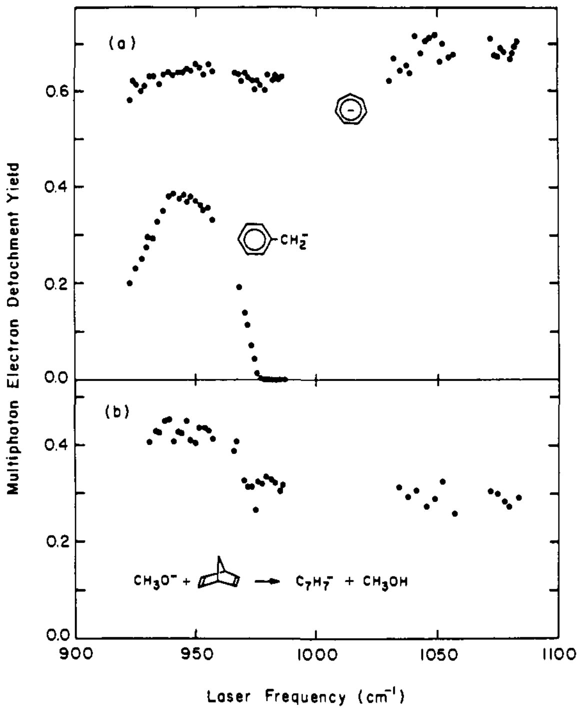
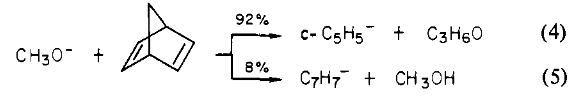


Figure 1. Infrared spectra of $C_7H_7^-$ isomers showing multiphoton electron detachment yield vs. laser frequency. (a) Spectra of cycloheptatrienyl (upper points) and benzyl (lower points) anions. Irradiation was for 200 ms at 24 W/cm^2. MED yield for benzyl anion was zero above 1000 cm^{-1}. (b) Spectrum of cycloheptatrienyl/benzyl mixture formed by deprotonation of norbornadiene by CH_3O^-. Irradiation was for 100 ms at 24 W/cm^2.

There is the possibility that the energy content of the ion influences the probability of multiphoton excitation and electron detachment.[8] This possibility is unlikely in the present case, and deuterium isotope exchange reactions in a flowing afterglow[19] apparatus support three distinct isomers.

Since three isomers are distinguished by their photodetachment spectra, the above experimental methodology may be used to identify $C_7H_7^-$ anions whose structures are uncertain. Reaction of CH_3O^- with norbornadiene results in cyclopentadienyl anion as the major product (reaction 4) although some $C_7H_7^-$ is produced in reaction 5. Norbornadiene is only weakly acidic,[20] however,



and deprotonation analogous to reaction 3 is endothermic by 23 kcal/mol in this case. Simultaneous structural rearrangement and deprotonation would make reaction 5 exothermic to form benzyl ($\Delta H_r = -39$ kcal/mol) or cycloheptatrienyl ($\Delta H_r = -12$ kcal/mol) anions, and these are considered the most likely structures for $C_7H_7^-$ in reaction 5.

When the reaction products are irradiated with the CW CO_2 laser, the spectrum of $C_7H_7^-$ in Figure 1b is obtained. Although the low resolution of the spectra introduces some uncertainty, the spectrum in Figure 1b appears to represent a mixture of cycloheptatrienyl and benzyl anions in a ratio of 1.5:1, respectively.[21] This unusual rearrangement to two different structural isomers has subsequently been observed in a flowing afterglow apparatus

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[19] Deprotonation of norbornadiene by NH_2^- results in $C_7H_7^-$ which exchanges up to three protons with ND_3 (Squires, R. R.; DePuy, C. H., private communication) indicating that deprotonation at the vinyl position (2, 3, 5, or 6) results in a stable bicyclic anion.

[20] Norbornadiene is easily deprotonated by NH_2^- but not by H^-, leading to an estimated acidity $D(H^+ - C_7H_7^-) = 402 \pm 5$ kcal/mol.

[21] Direct comparison of the yields in Figure 1a,b is complicated by the moderately high pressure (5×10^{-6} torr) required to observe reaction 5. The MED yields are empirically corrected for collisional deactivation effects to obtain the reported composition of the $C_7H_7^-$ signal.

for the reaction of hydroxide ions with norbornadiene, yielding benzyl and cycloheptatrienyl anions as products.[22] In the flowing afterflow apparatus, structural isomers are distinguished by successive proton-exchange reactions with CH_3OD or D_2O.[23]

Multiphoton electron detachment represents a convenient general method for obtaining infrared spectra of negative ions because most photodetachment thresholds lie well below thresholds for photodissociation. In addition, stable negative ions may be formed by proton transfer from an enormous number of molecules with labile protons. With the development of moderately intense (>1 W/cm^2) lasers in other regions of the infrared, more extensive spectra will be obtained, yielding detailed information about structure and bonding in molecular ions. With sufficient laser intensities it is anticipated that recording infrared spectra may become a routine application of mass spectrometry.

Acknowledgment. We gratefully acknowledge stimulating discussions with Dr. R. R. Squires. This work was supported in part by the President's Fund of the California Institute of Technology and the U. S. Department of Energy.

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Periodic Trends in Transition Metal-Hydrogen, Metal-Carbon, and Metal-Oxygen Bond Dissociation Energies. Correlation with Reactivity and Electronic Structure

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The strengths of bonds formed between transition metals and various substituent groups are of fundamental importance in the areas of surface chemistry, organometallic chemistry, and catalysis. The scarcity of such thermodynamic information has led us to develop new experimental methods for the determination of the thermochemical properties of organometallic species.[2-8] Most important are ion beam experiments in which an examination of the translational energy dependence of endothermic reactions yields bond energies of product species.[5-8] Studies of the general process 1, where M^+ is an atomic metal ion and $R_2 = H_2, C_2H_6, C_2H_4$,

$$M^+ + R_2 \rightarrow MR^+ + R \qquad (1)$$

and O_2, provide the bond energies of metal hydrides, methyls, carbenes, and oxides summarized in Table I.[9] Experimental techniques and methods of analysis have been detailed in previous work.[5-7] The results presented in Table I represent the first such data base involving transition-metal species. A close examination of these data reveals a correlation of metal–ligand σ bond energies with the electronic configuration of the metal ion and permits some interesting comparisons of metal ion thermochemistry and reactivity.

Table I. Summary of Metal–Ligand Bond Dissociation Energies[a,b]

	Cr^+–R	Mn^+–R	Fe^+–R	Co^+–R	Ni^+–R	Zn^+–R
R = H	35 ± 4	53 ± 3[c]	58 ± 5	52 ± 4	43 ± 2	60[d]
R = CH_3	37 ± 7	71 ± 7[c]	68 ± 4	61 ± 4	48 ± 5	67 ± 1[e]
R = CH_2	65 ± 7	94 ± 7	96 ± 5	85 ± 7	86 ± 6	
R = O	77 ± 5	57 ± 3	68 ± 3	65 ± 3	45 ± 4	
promotion energy[f]	34.2	0	0	9	24.0	0

[a] All data in kcal/mol at 298 K. [b] All values from this study or ref 5–8 unless otherwise indicated. [c] These values are somewhat uncertain due to difficulties in interpretation of the data; the results for MnH^+ agree within experimental error with those reported in ref 4. [d] Reference 12. [e] Reference 14. [f] Promotion energy from lowest state derived from the $3d^n$ configuration to the lowest state derived from the $3d^{n-1}4s^1$ configuration. Values from reference 10.

Figure 1 shows the correlation of M^+–R bond energies for R = H and CH_3 with the difference in energies between the metal ion ground state and the lowest state derived from the $3d^{n-1}4s^1$ configuration.[10] For Mn^+, Fe^+, and Zn^+, the $3d^{n-1}4s^1$ configuration gives rise to the ground state, while Cr^+, Co^+ and Ni^+ have a ground state derived from the $3d^n$ configuration. The correlation suggests that formation of the first metal–ligand σ bond involves mainly the 4s orbital on the metal. A similar conclusion was reached by Scott and Richards[11] in a survey of experimental and theoretical results for the neutral metal hydrides, ScH through FeH. They suggest that the $3d^{n-1}4s^1$ configuration of the metal gives rise to the ground state of the hydride and that the d electrons are largely nonbonding.

If the noted correlation holds across the periodic table, bond energies of other transition metals can be predicted. Indeed, Sc^+, Ti^+, and V^+ should all have strong hydride and methyl bonds since they have promotion energies of 0, 0, and 7.4 kcal/mol, respectively.[10] Copper ions are predicted to have weak bonds (~15 kcal/mol) since the promotion energy is 63 kcal/mol.[10] Concerning other rows of the periodic table, the only available bond energies are for the group 2B metals Zn, Cd, and Hg.[12-14] Metal ion hydride bond energies for Cd^+ and Hg^+ are 48 and 70 kcal/mol,[13] respectively, while the methyl bond energies are 54 and 68 kcal/mol,[14] respectively. Since Cd^+ and Hg^+ both have $d^{10}s^1$ ground states, these values clearly do not fit the correlation of Figure 1. The group 8 metal ions Rh^+ and Pd^+ have promotion energies of 73 and 72 kcal/mol,[10] respectively, from their ground states (derived from $3d^n$ configurations) to the lowest states derived from the $3d^{n-1}4s^1$ configuration. Metal hydrogen bond energies of these species would be very small if the above correlation were to hold. However, ICR studies of the reactions of Rh^+ suggest a reasonably strong Rh^+–H bond,[15] which may imply that the

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