at 185 nm);[44] (3) adding Cl⁻ lowers Φ_r (Cl⁻ absorbs strongly at 185 nm);[31] (4) photolysis in deuterated alcohol does not alter Φ_r (deuterated alcohols absorb even less than the hydrogen-containing alcohols at 185 nm);[45] and (5) the action spectrum indicates that the increase in Φ_r parallels the primary absorbing species, the ruthenium complex.

We have demonstrated the utility of 185-nm radiation to uncover enhanced photoredox behavior which would not be observed by simply photolyzing at 214 or 229 nm. Mechanisms have been proposed to account for the absence of photoreduction in the absence of alcohol. Further, we have evidence to suggest an unusual "hydrogen-abstraction" reaction of the 2-propanol radical, catalyzed by ruthenium.

The instability of the radicals involved in this study prevents their further identification at this stage. It is our intention to demonstrate further evidence of the

(44) J. Barrett and A. L. Mansell, Nature (London), 187, 138 (1960).
(45) Private communication, Professor M. Fox.

enhanced photoredox behavior of metal complexes at 185 nm by choosing complexes which are capable of producing stable one-electron reduction products of the ligands.

Ion Cyclotron Resonance Photodissociation Spectroscopy Spectra of Substituted Benzenes

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Abstract: The first extensive series of photodissociation spectra are reported for a group of mono- and disubstituted benzene compounds between 0.2 and 0.8 μ. For each ion at least two distinctive and relatively sharp photodissociation peaks are observed. Comparison of the photodissociation spectra with their corresponding photoelectron spectra suggests that the two techniques are comparable in the expected way and that the ions observed by the two techniques are structurally similar. Substantial differences in the spectra produced by the two techniques are observed. These differences can be of potential value in interpreting both types of spectra.

Since observation of the photodissociation of CH_3Cl^+ by ion cyclotron resonance spectroscopy,[2] examinations of light-induced dissociation and reactions of a number of gas phase ions have been reported.[2-7] Icr spectroscopy has proved to be a convenient method for observing these processes under low pressure ($10^{-9}-10^{-7}$ Torr) steady state conditions where photon-induced processes can readily compete with other ion–molecule reactions.

Early work in this area has indicated that the cross section for photodissociation of gas phase cations is energy dependent.[2] A study of isomeric $C_7H_8^+$ ions by Dunbar and Fu[6] confirms that dissociation maxima may occur in the visible region of the spectrum for some ionic species. This has prompted the present study of the photodissociation spectroscopy (pds) of a wide range

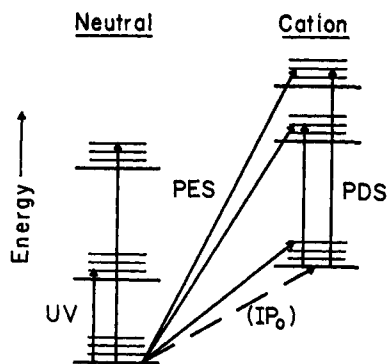(1) Alfred P. Sloan Fellow.
(2) R. C. Dunbar, J. Amer. Chem. Soc., 93, 4354 (1971).
(3) J. M. Kramer and R. C. Dunbar, J. Chem. Phys., 58, 1266 (1973).
(4) J. M. Kramer and R. C. Dunbar, J. Amer. Chem. Soc., 94, 4346 (1972).
(5) R. C. Dunbar, J. Amer. Chem. Soc., 95, 472 (1973).
(6) R. C. Dunbar and E. Fu, J. Amer. Chem. Soc., 95, 2716 (1973).
(7) R. C. Dunbar, J. Amer. Chem. Soc., 95, 6191 (1973).

of substituted benzene cations in the near uv and visible regions of the optical spectrum.

Previous studies of ions produced by electron impact and trapped for long periods in the icr spectrometer have been interpreted as indicating that the ion energy is probably near thermal.[7] Thus, addition of an unreactive quenching gas such as N_2 or CH_4 has no effect on the photodissociation rate constant (other than that produced by pressure changes) in a number of systems.[4,7] The absorption of near uv or visible light by ions in these photodissociation experiments can reasonably be assumed to involve excitation of the ion from the thermalized electronic ground state to some excited electronic energy level, probably with vibrational excitation within that level. A photodissociation spectral peak indicates an optical absorption peak for the cation and is governed in part by the Franck–Condon overlap of the two electronic energy states, as in other electronic excitation processes.

A fruitful comparison may be made between photodissociation spectroscopy and uv photoelectron spectroscopy, in which the thermal neutral molecule is excited *directly* to an excited electronic energy level of the *ion*

Figure 1. The pes vertical electronic excitation process involves neutral ionization to an excited ion state while the pds process involves direct ion excitation. The uv neutral excitation process is included for comparison.
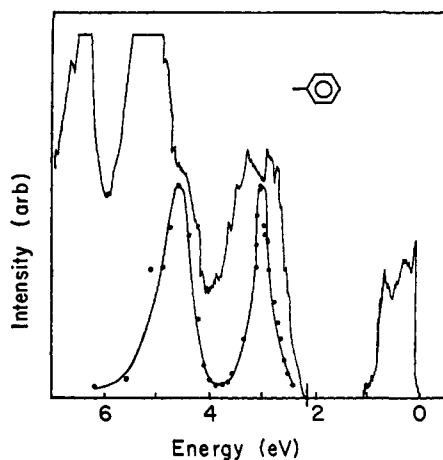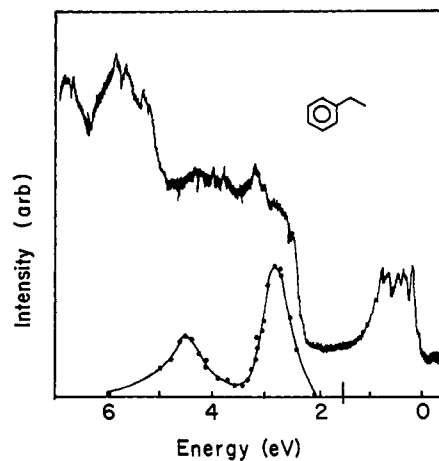

Figure 2. The photodissociation spectra (●) and the pes spectra of toluene are plotted on an arbitrary intensity scale to facilitate comparison. The pes adiabatic first ionization potential is assigned a value of zero on the pds energy scale.

Figure 3. The photodissociation spectra (●) and the pes spectra of ethylbenzene are plotted on an arbitrary intensity scale to facilitate comparison. See the caption to Figure 2.

Figure 4. The photodissociation spectra (●) and the pes spectra of n-propylbenzene are plotted on an arbitrary intensity scale to facilitate comparison. See the caption to Figure 2.

by uv irradiation. Assuming that the resultant ions of the pes and pds processes are structurally similar, the pes absorption spectrum should be similar to the photodissociation spectrum but displaced from the pds spectrum by the additional energy required in pes to ionize the neutral molecule to the thermal ion. This of course is the adiabatic ionization potential for that ion.[8] These two excitation processes are shown in Figure 1, where the vertical electronic excitation process is shown for both pes (neutral ionization) and pds (ion excitation). The uv neutral excitation process is also included for comparison.
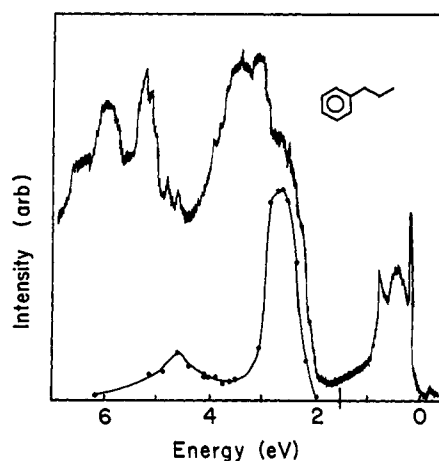
The various excited ionic states reached in pes result from promotion of the hole through the filled levels of the molecule. In pds there will be both this type of state and that resulting from unpaired electron promotion upward through the unfilled levels of the ion. Thus, while pds peaks may occur at the same energy as pes peaks (hole promotion type excited states), pds peaks with no corresponding pes peaks may identify the electron promotion type excited states (if in fact these latter states lead to ion dissociation).

In addition to the condition that the excited ion produced by these two processes be structurally similar be-

fore comparison can be made, it is apparent that, as in any light absorption process, symmetry conditions may impose selection rules on the simple Franck–Condon overlap integral.[9] Neutral ionization to electronically excited ion states and direct optical excitation to these same states would be expected to have differing allowed transitions. Thus, while the pes and pds processes are expected to be comparable, they are not expected to be identical. These differences are of potential value in interpreting both types of spectra and may aid in unraveling ionic excitation processes and ion structures.

While the photodissociation spectrum reflects the optical spectrum of the ion, it is worth emphasizing that it is an indirect approach, and the appearance of a peak in the pds spectrum requires both an optical absorption peak and a subsequent available dissociation mechanism for the excited ion. This implies, first, that no photodissociation peak should be anticipated below the thermodynamic threshold[7] for the dissociation of the ion and, second, that failure to observe a photodissociation peak for a given excited state of the ion can always be due to the lack of an allowed dissociation mechanism competitive in rate with other deexcitation processes.

(8) D. W. Turner, et al., "Molecular Photoelectron Spectroscopy," Wiley-Interscience, London, 1970.

(9) G. Herzberg, "Electronic Spectra of Polyatomic Molecules," Van Nostrand, Princeton, N. J., 1966.

Figure 5. The photodissociation spectra (●) and the pes spectra of *n*-butylbenzene are plotted on an arbitrary intensity scale to facilitate comparison. See the caption to Figure 2.
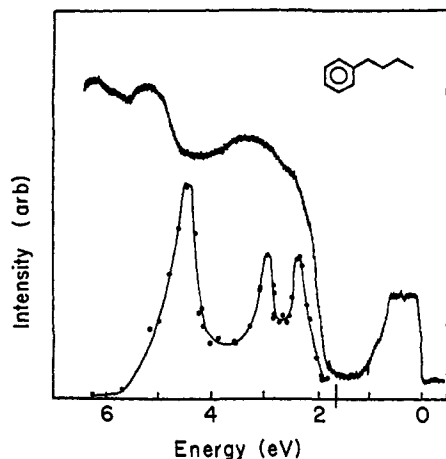

Figure 6. The photodissociation spectra (●) and the pes spectra of *tert*-butylbenzene are plotted on an arbitrary intensity scale to facilitate comparison. See the caption to Figure 2.

Experimental Section

The present experimental arrangement is similar to that described previously,[7] with only minor changes. The Varian ICR-9 spectrometer, fitted with the standard "square" cell, was used with a trapping voltage of 2–3 V and near zero drift potentials. The marginal oscillator frequency was varied between 150 and 307 KHz in order to obtain good trapping fields between 10 and 12 kG. Neutral gas pressures were varied between 5×10^{-8} and 2×10^{-7} Torr so that comparable ion lifetimes could be obtained. Electron energies were usually 1–2 eV above the reported appearance potentials.

Double resonance ejection signals were applied to the analyzer region of the cell. Substantial ion ejection begins to be apparent at amplitudes less than 0.03 V, but for quantitative ejection of an ionic species, amplitudes greater than 0.10 V are necessary. Since severe interference between the marginal oscillator and the double resonance oscillator begins above 0.10 V, it was not always possible to assure quantitative ion ejection. In a few cases this leads to some ambiguity in the results.

Light was generated by a 2.5-kW xenon arc lamp and wavelength selected by a Schoeffel monochromator. The monochromator slit width was 4 mm giving a nominal bandpass (full width at half-maximum) of 133 Å while the grating was blazed at 3000 Å. Relative light intensity as a function of wavelength was measured using an Eppley thermopile, and the measured photodissociation rate constants were corrected inversely to the relative light intensity at each wavelength. The relative calibration data were assumed constant over the several weeks of experimentation and were probably good to ±5%. Near 2000 Å, however, severe tailing off of the light intensity made correction less certain (±15% below 2200 Å).

The compounds were not purified other than by freezing and degassing at the spectrometer inlet. Each sample was, however, checked for impurities in the ion spectrum at high-electron energy.

The photoelectron spectra for the simple alkylbenzenes were taken from Turner.[8] All the other spectra were obtained from a Varian photoelectron spectrometer with a uv source. These spectra were scanned from threshold to 20 eV at high resolution and then scanned from threshold to 14 eV on an expanded scale to aid in correlating the adiabatic threshold with zero on the icr–pds energy scale.

Results

Each ion was scanned from 2000 to 8000 Å. The ratio of the parent ion signal decrease with the light on to the total parent ion signal with the light off (relative photodissociation rate constant)[7] was corrected for light intensity and plotted as a function of wavelength. Photoreactions as well as dark reactions of the reactants and the photoproducts were examined by the double resonance technique in each region of light absorption. In none of the cases was the production of parent ion by any of the secondary ions detected. (Parent production by a secondary process would clearly invalidate
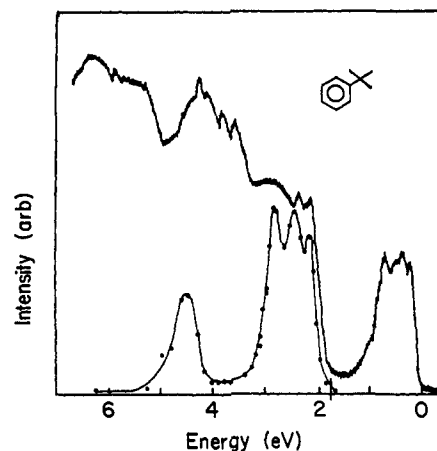
analysis of the photodissociation results along the lines followed here, if not accounted for.)[7]

Photodissociation. Only one photodissociation pathway predominates for each of the ions examined. These ions can be easily classified into three categories. Group I is comprised of those ions which dissociate to to $C_7H_7^+$ as the primary ionic photofragment. This is the largest group and includes toluene, the mono- and disubstituted alkylbenzenes (except *tert*-butylbenzene), and the *p*-halotoluenes (except *p*-fluorotoluene). Group I is characterized by the reaction

$$P^+ \xrightarrow{h\nu} C_7H_7^+ + S \qquad (1)$$

where P^+ is the electron impact produced parent ion and S is the appropriate neutral fragment for mass balance.

Group II ions are those which lose a hydrogen atom upon photodissociation to give a $(P - 1)^+$ secondary ion. This group includes toluene (by the nature of the grouping toluene is common to both groups I and II), as well as *p*-fluorotoluene and the substituted anilines. The characteristic reaction is

$$P^+ \xrightarrow{h\nu} (P - 1)^+ + H \qquad (2)$$
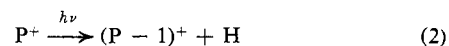
Due to the limited number of ions studied, one ion appears to have a unique dissociation process and has been included in group III. The photodissociation of *tert*-butylbenzene is characterized by the loss of CH_3.

$$C_{10}H_{14} \xrightarrow{h\nu} C_9H_{11}^+ + CH_3 \qquad (3)$$
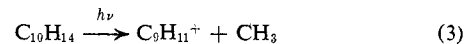
Below 4000 Å additional wavelength-dependent processes occur to an appreciable extent. At present these are not fully understood, but it is clear that the parent ion is not regenerated by these secondary reactions.

Secondary Reactions. The secondary reactions of the substituted alkylbenzenes have been covered in detail elsewhere; however, the *p*-halotoluenes have not been examined before. Double resonance studies of the *p*-halotoluenes indicate that the photodissociation product, $C_7H_7^+$, reacts with neutral parent to form a $(P - 1)^+$ ion which in turn reacts with the parent to form $C_8H_9X^+$. This excludes *p*-fluorotoluene where the $(P - 1)^+$ ion is the only secondary ion present. Direct photon-induced reaction of the parent ion with the neutral parent molecule of the form
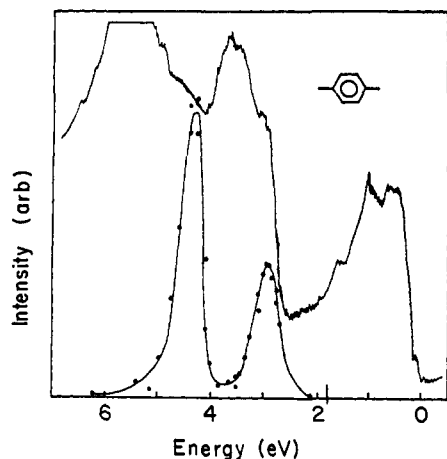
$$C_7H_7X^+ + C_7H_7X \xrightarrow{h\nu} C_8H_9X^+ + C_6H_5X \qquad (4)$$

Dymerski, Fu, Dunbar / ICR–PDS Spectra of Substituted Benzenes

Figure 7. The photodissociation spectra (●) and the pes spectra of p-xylene are plotted on an arbitrary intensity scale to facilitate comparison. See the caption to Figure 2.

Figure 9. The photodissociation spectra (●) and the pes spectra of p-chlorotoluene are plotted on an arbitrary intensity scale to facilitate comparison. See the caption to Figure 2.
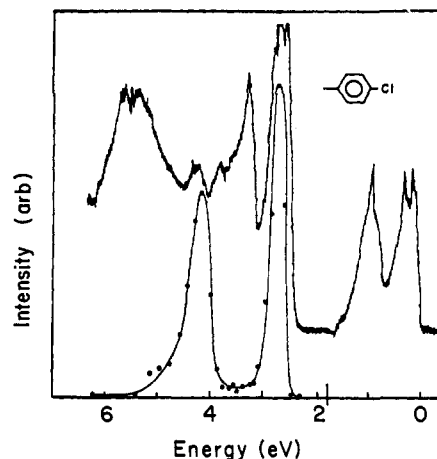

Figure 8. The photodissociation spectra (●) and the pes spectra of p-fluorotoluene are plotted on an arbitrary intensity scale to facilitate comparison. See the caption to Figure 2.

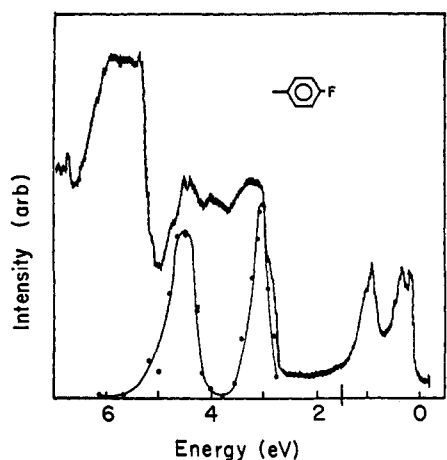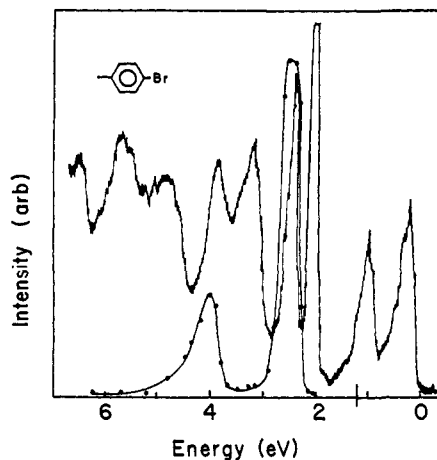
Figure 10. The photodissociation spectra (●) and the pes spectra of p-bromotoluene are plotted on an arbitrary intensity scale to facilitate comparison. See the caption to Figure 2.

cannot be completely ruled out, but double resonance ejection of $C_7H_7^+$ reduces the $C_8H_9X^+$ signal to near zero, indicating that the photoreaction of eq 4 is at most a minor reaction.

Spectra. Figures 2–14 show the photodissociation spectra for each of the ions studied. Table I groups the ions according to their photodissociation pathway. For each of the ions examined, at least two distinct peaks are apparent between 2 and 6 eV (n-butylbenzene and tert-butylbenzene show additional structure). The vertical dissociation energy for each peak is listed in Table I, where E_{v_i} is the energy of the maximum in the dissociation rate constant for the lower energy peak.

While the signal intensity of each spectrum has been arbitrarily normalized to facilitate comparison with the photoelectron spectrum, the relative peak heights within each photodissociation spectrum have been found to be nearly independent of experimental conditions (for a given pressure) and reproducible within a few per cent. The energy axis of each pes spectrum was normalized by assigning the adiabatic first ionization potential of the neutral to the value of zero on the pds energy scale. This was done graphically and introduces an uncertainty in the pes energy axis of less than 0.2 eV for most of the ions studied. The photodissociation energy axis is, of course, absolute.

Table I. Ion Photodissociation Data

Parent ion	$E_{v_1}{}^a$	$E_{v_2}{}^a$	$\Delta H_{thermal}{}^b$
Group I:	$P^+ \xrightarrow{h\nu} C_7H_7^+ + S$		
Toluene	2.97	4.55	2.13
Ethylbenzene	2.78	4.50	1.59
n-Propylbenzene	2.65	4.57	1.49
n-Butylbenzene	2.35, 2.90	4.70	1.63
p-Xylene	2.90	4.30	2.03
p-Chlorotoluene	2.70	4.25	1.78
p-Bromotoluene	2.40	4.00	1.20
p-Iodotoluene	2.08	3.95^c	0.76
m-Methylanisole	2.95^c	4.43	2.02
Group II:	$P^+ \xrightarrow{h\nu} (P - 1)^+ + H\cdot$		
Toluene			
p-Fluorotoluene	2.96	4.50	1.48
p-Toluidine	2.95	4.27	1.30
N,N-Dimethylaniline	2.78	4.60	3.69 (?)
Group III:	$C_{10}H_{14}^+ \xrightarrow{h\nu} C_9H_{11}^+ + CH_3$		
tert-Butylbenzene	2.15, 2.39, 2.83	4.50	1.24

^{a} Vertical photodissociation energy in eV (±0.05 eV unless otherwise stated). ^{b} All ΔH_f data taken from ref 10. ^{c} ±0.1 eV.

Discussion

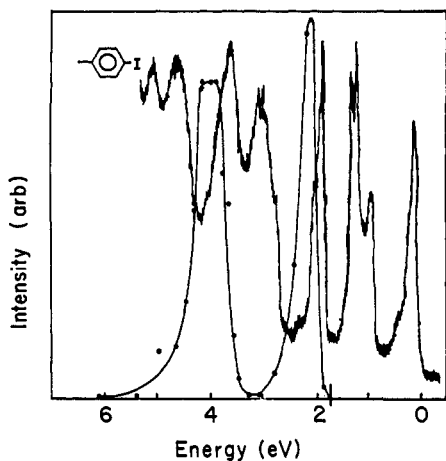Due to the severe overlapping of the photoelectron peaks above the first few ionization potentials, it is ap-

Figure 11. The photodissociation spectra (●) and the pes spectra of p-iodotoluene are plotted on an arbitrary intensity sacle to facilitate comparison. See the caption to Figure 2.

Figure 13. The photodissociation spectra (●) and the pes spectra of m-methylanisole are plotted on an arbitrary intensity scale to facilitate comparison. See the caption to Figure 2.

Figure 12. The photodissociation spectra (●) and the pes spectra of p-toluidine are plotted on an arbitrary intensity scale to facilitate comparison. See the caption to Figure 2.
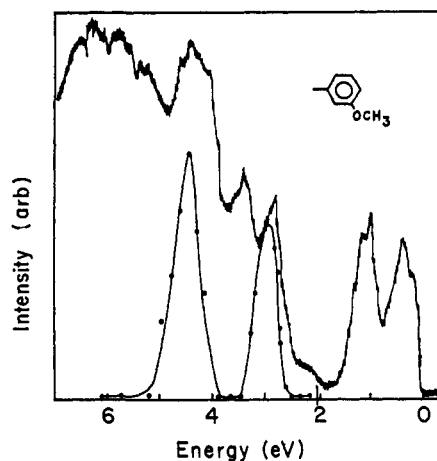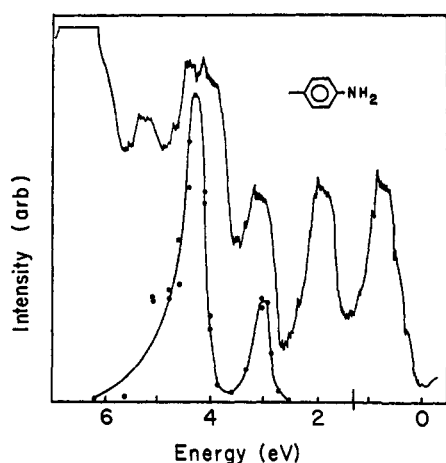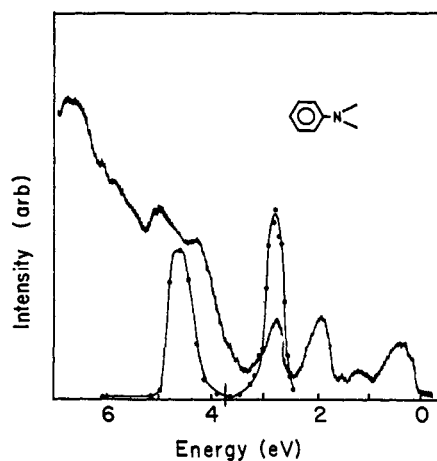

Figure 14. The photodissociation spectra (●) and the pes spectra of N,N-dimethylaniline are plotted on an arbitrary intensity scale to facilitate comparison. See the caption to Figure 2.

parent that numerical comparison of the vertical excitation energies is in many cases not practical. For the present purpose of an initial comparison, however, a graphical comparison will be sufficient.

Three trends are apparent for the ions examined. First, for each pds peak observed, there is a corresponding pes peak. Clear examples of this are the halotoluenes. E_{v_2} of n-butylbenzene is the least clear case, where the high-resolution pes spectrum in the region of E_{v_2} is unresolved and may or may not contain peaks corresponding to the photodissociation peaks. Second, there are numerous pes peaks which have no corresponding pds peak. Clear examples of this are the pes peaks (3–3.5 eV) of the halotoluenes and the 3.5 eV peak of m-methylanisole. Third, no unambiguous examples were found for pds peak occurrence without a corresponding pes peak. (Admittedly this is often hard to determine in the high energy range of the pes spectra.) This suggests that either electron promotion to unfilled ion levels is not significant or at least does not lead to detectable ion dissociation.

One of the principal applications of the ion photodissociation technique has been the establishment of structural differences among long-lived gas phase cations.[6] The striking difference between the pds

spectra of toluene and cycloheptatriene cations has been cited[6] as evidence that they do not rearrange to a common structure. Further, the excellent correspondence between the photodissociation spectrum of toluene and the pes spectrum of toluene provides strong (though not absolute) evidence that the toluene parent cation does in fact retain the toluene structure. While spectra of other possible isomers of the other ions examined in this work are not yet available for comparison, the excellent correspondence with the pes spectra for all these ions is good evidence that in general these substituted benzene compounds do not undergo major structural reorganization, upon electron impact ionization near threshold. As always in icr trapped ion studies, this structural information refers to ions which are typically trapped and thermalized in the spectrometer for several seconds.

It is noteworthy that for the halotoluene cations, the lowest photodissociation peak apparently corresponds to an ion excitation energy in the region commonly assigned to a state with a vacancy in the nonbonding halogen orbitals. The energy of this transition shows a progressive shift to longer wavelengths by about 0.3 eV for a substitution of any halogen by the next heavier

halogen. As Figures 8–11 indicate, this is in full accord with the expectation based on the pes spectra.

Thermodynamic Threshold. The thermodynamic thresholds for the observed photodissociation processes (calculated from reported heats of formation)[10] are listed in Table I and marked (vertical slash) in each ion spectrum. For most of the ions examined there was only one heat of formation available[10] for the photodissociation product ion of the observed (substituted benzene) empirical formula. It was necessarily assumed that the product ion of the photodissociation process was of the same isomeric configuration as that observed in the literature.[10] With one exception (N,N-dimethylaniline) no photodissociation peaks were observed below the calculated thresholds.

In the case of N,N-dimethylaniline the only available heat of formation for the observed (P − 1) photodissociation product is 217 kcal mol⁻¹ (obtained by photoionization).[11] This yields a heat of dissociation of 3.69 eV, which is ∼1.4 eV *above* the onset of the lowest observed pds peak. This implies that the reported heats of formation are incorrect by approximately 32 kcal mol⁻¹ or that the ions of the observed photodissociation (parent or product) are of a different isomeric form than that obtained by the photoionization process.[11] Rearrangement of the observed parent ion seems unlikely in view of the strong correspondence of the pds and pes peaks for N,N-dimethylaniline as seen in Figure 14.

The heat of dissociation can be calculated for alterna-

tive dissociation pathways for most of the ions examined. In each case the alternative path is more endothermic by at least 0.5 eV. Even though this alternative threshold may be within the energy range of excitation (<6 eV), the ion essentially always dissociates along the lower energy path. This is in accord with the predictions of the quasiequilibrium theory of unimolecular decay and is also in accord with the observed most probable fragmentation process for all of these ions from mass spectroscopy.[12]

Conclusion

The present results represent the first extensive series of photodissociation spectra reported for the wide range of energies used. The striking and distinctive spectral peaks found for these ions have potential value in understanding the electronic properties of the ions. The degree of correspondence found between the photodissociation results and the pes spectra is sufficient to give confidence that the two techniques are indeed comparable in the expected way and that the ions examined by the two techniques are structurally similar. The substantial differences in the spectra produced by the two techniques clearly provide opportunities for fruitful comparison.

(10) J. L. Franklin, *et al., Nat. Stand. Ref. Data Ser., Nat. Bur. Stand.*, No. 26 (1969).

(11) M. Akopyan and F. Vilesov, *Dokl. Akad. Nauk SSSR*, **158**, 1386 (1964).

(12) A. Cornu and P. Massot, "Compilation of Mass Spectral Data," Heyden and Son Ltd., Great Britain, 1966.

Platinum and Palladium Complexes Formed by Chelative Addition of Amines to Isocyanides

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Contribution from the Department of Chemistry, University of California, Davis, California 95616. Received January 11, 1974

Abstract: The addition of amines to coordinated isocyanides has been explored as a method of preparing new chelating ligands. The reaction of amidines and 2-aminopyridine with Pt(CNCH₃)₄²⁺ produces complexes of the type (chelate)Pt(CNCH₃)₂²⁺,⁺ containing bidentate ligands which utilize one imine nitrogen donor and one trigonal carbon donor. Biacetyldihydrazone reacts with M(CNCH₃)₄²⁺ (M = Pd, Pt) to produce a bidentate ligand which contains two trigonal carbon donors, one of which is incorporated into an imidazole ring. The addition of 2,6-diaminopyridine to M(CNCH₃)₄²⁺ produces a tridentate ligand with one pyridine nitrogen donor and two trigonal carbon donors. These new complexes have been isolated and characterized by elemental analysis, conductivities, and infrared and proton magnetic resonance spectra. The properties of these complexes and the related cations obtained by the addition of hydrazine to M(CNCH₃)₄²⁺ are compared. The new chelating ligands undergo reversible loss (or gain) of protons and the sites of these reactions have been elucidated. The electronic spectra of these complexes in solution are sensitive to the site of the proton transfer. In the solid state certain of these complexes exhibit electronic absorptions which are not found in their solutions. It is suspected that these additional absorptions result from the formation of stacks of complexes in the solid state so that chains of metal atoms result. In general the new chelating ligands and their complexes are very stable to acidic and oxidizing conditions, and it has been possible to oxidize some Pt(II) complexes to Pt(IV) species by the addition of halogens.

Although considerable effort has been expended on the design and synthesis of chelating ligands,[1] the

(1) For examples see D. St. C. Black and A. J. Hartshorn, *Coord. Chem. Rev.*, **9**, 219 (1973).

number of chelating ligands involving simple carbon donors (excluding, that is, π-complexes) is relatively small. In this report we develop the use of the reaction between isocyanide ligands and nitrogen bases for the