

Electron attachment by haloalkenes and halobenzenes

James K. Olthoff, John A. Tossell, and John H. Moore

Department of Chemistry, University of Maryland, College Park, Maryland 20742

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Electron transmission spectra and mass spectra of negative ions from dissociative electron attachment have been obtained for four series of halogenated alkenes: vinyl halides, chloroethylenes, halobenzenes, *para*-dihalobenzenes. The stabilizing effect of halogen substituents upon anion state energies is obvious. Systematic observations permit assignment of Σ and Π anion states. Dissociative attachment usually proceeds through the Π anion state. An enormous enhancement of the cross section for dissociative attachment of threshold electrons is observed in some cases.

In the past three decades, many scientists have studied the processes of electron capture and dissociative electron attachment to halogenated alkenes. There are a variety of reasons for such great and continuous interest. From a somewhat theoretical point of view, haloethylenes and halobenzenes serve as models of substitutional effects on unsaturated systems. Electron capture by these molecules involves the π^* molecular orbitals and thus serves as a probe of the effect of substitution upon π^* orbital energies. On the practical side, electron capture methods are useful for the detection of organic halides in chromatographs and other analytical instruments. Dissociative attachment is an important channel for the degradation of halocarbons in the atmosphere in high voltage apparatus. It is also presumed that γ radiation degrades organic halides in condensed phases as a result of dissociation arising from capture of thermal electrons that are produced by the action of the radiation on the solvent. Halocarbons have found use as moderators of, and sinks for, low energy electrons. In the final analysis, the reason halogenated alkenes have received so much attention is because their electron capture cross sections are very large and because dissociation is a prominent mode of decay of their temporary anions.

Electron capture has been studied using both swarm and beam techniques with energy resolutions of 40 meV to 0.5 eV, and under density regimes ranging from single collision to viscous flow conditions. The products of dissociation have been detected using both mass spectrometric and chromatographic techniques. Despite all the study of these processes in the halogenated alkenes, there are many features which are not understood. This is due at least in part to the difficulty of comparing the results of one type of experiment with those of another. The problem has on many occasions been further exacerbated by a rather piecemeal selection of targets for study. Thus trends within an homologous series of molecules are difficult to discern.

In the present work, electron transmission spectroscopy is employed to determine the electron affinities, or attachment energies, for electron capture under single collision conditions. The mass and kinetic energy of fragments of dissociative attachment are determined by time-of-flight mass spectrometry. This combination of instruments in a single experiment provides the greatest precision currently available. We have undertaken the investigation of complete series of halogenated alkenes: the vinyl halides (vinyl fluoride

through vinyl iodide), the chloroethylenes (vinyl chloride through tetrachloroethylene), the halobenzenes, the *para*-dihalobenzenes. For many individual members of these series there are data in the literature on electron capture and dissociative attachment. Nevertheless, obtaining complete data sets under similar experimental conditions and presenting these results all in one place is worthwhile.

The electron transmission spectrometer employed is similar to that designed by Stamatovic and Schulz.¹ This device measures the change in the total cross section for electron scattering as a function of electron energy. The output is the first derivative of transmitted current as a function of energy, thus spectra from this instrument focuses attention upon sharp changes of the scattering cross section. Abrupt changes characterize resonant scattering due to the temporary formation of a negative ion at a particular energy. This resonant energy is termed an attachment energy. The attachment energy can be identified as the negative of the vertical electron affinity. The energy resolution is about 40 meV, typical of modern electron spectrometers.

The negative ion products for dissociative attachment are detected by a time-of-flight spectrometer. Negative ion fragments drift out of the collision chamber with the translational energy of dissociation. These ions are accelerated by precisely 20 eV before arriving at a gate at the entrance to a 40 cm flight tube. The gate is opened for 100 ns at a 5 kHz rate. The gate pulse is sufficiently short that the fragment mass can be determined with a resolution better than 1 amu and the fragment velocity can be determined with a resolution better than 100 meV. This latter feature did not play an important part in the present studies since no ionic fragment of the dissociative attachment to the halogenated alkenes was observed to have translational energy in excess of 100 meV.

VINYL HALIDES

Electron transmission spectra

By way of introduction to electron transmission spectroscopy (ETS), derivative electron transmission spectra of the vinyl halides are shown in Fig. 1. Two low energy features are apparent in each spectrum and indeed in most electron transmission spectra. These are (1) a turn-on spike which is simply the derivative of the step associated with the abrupt turn-on of current near 0 eV, and (2) a "retarding

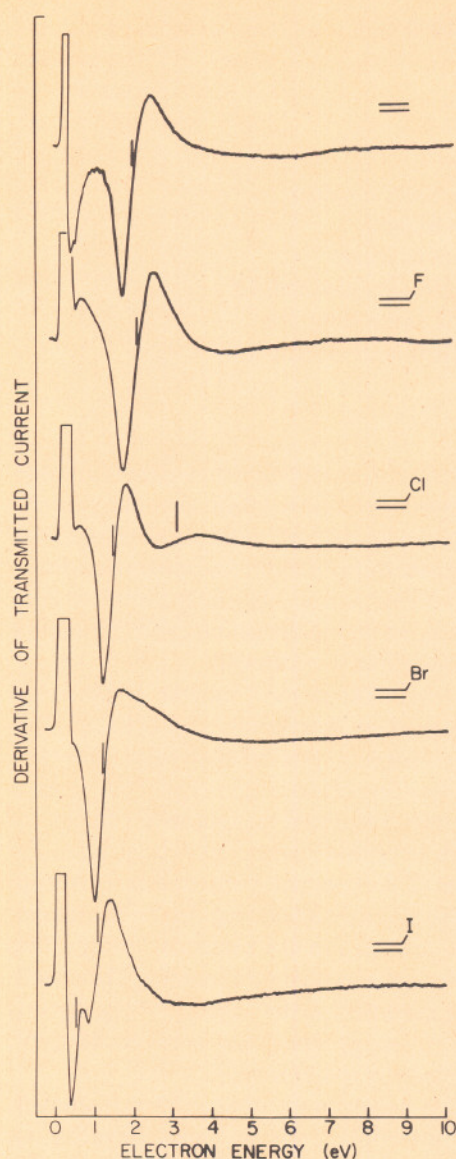


FIG. 1. Derivative electron transmission spectra of the vinyl halides. The positions of temporary negative ion resonances are indicated. The structure at threshold is discussed in the text.

cusp"² which is the relatively sharp minimum following on the heels of the first feature. The turn-on feature is sharp if the instrument is properly adjusted to provide maximum current from near 0 eV upwards, and if the bandpass of the electron monochromator is narrow. The turn-on feature is characteristically broadened if the target molecule possesses an anion state whose energy is slightly below or slightly above 0 eV. The cusp is a well-known instrumental artifact whose position depends upon the tuning of the instrument.

In the spectrum of ethylene, as well as in all of the vinyl halide spectra, there is a prominent feature between 1 and 2 eV. This is the derivative of the sudden decrease in transmitted current due to resonant electron scattering associated with temporary formation of the $^2\Pi$ anion state due to the electron capture into the π^* orbital associated with the C=C double bond.³⁻⁸ By convention, the attachment energy corresponding to such a feature in the derivative electron transmission spectrum is the energy at the point vertically mid-

way between the minimum and maximum of the spectral feature. A second resonance associated with electron capture into a carbon-halogen σ^* orbital⁹ is more or less evident in the spectra of all the vinyl halides. In vinyl fluoride the σ^* resonance is very broad due to the high energy and short life of the $^2\Sigma$ anion state in vinyl fluoride. The σ^* resonance decreases in energy and increases in sharpness upon descent of group VII. The σ^* resonance merges with the π^* resonance in vinyl bromide and is lower in energy than the π^* resonance in vinyl iodide (*vide infra*). Electron transmission spectra have previously been reported for vinyl fluoride^{4,8} and vinyl chloride.⁹ The results of the various measurements agree to within 50 meV.

The electron transmission data for the vinyl halides is collected in a correlation diagram in Fig. 2. Also included are cation state energies from photodetachment of electrons from the occupied valence orbitals.¹⁰ The correlation diagram implies an independent electron model for the valence orbitals. Thus the measured energies are associated with the eigenvalues of the orbital into which an electron is captured or from which an electron is ejected. Such a model, although not entirely accurate, has historically been productively applied by photoelectron spectroscopists in assuming the validity of Koopman's theorem when interpreting their data. The data imply that the π^* orbital is destabilized upon substitution of fluorine on ethylene. However, proceeding down group VII, the π^* orbital is stabilized relative to ethylene. The destabilization of π^* in vinyl fluoride and the concomitant stabilization of the occupied, predominantly F2p_z is at-

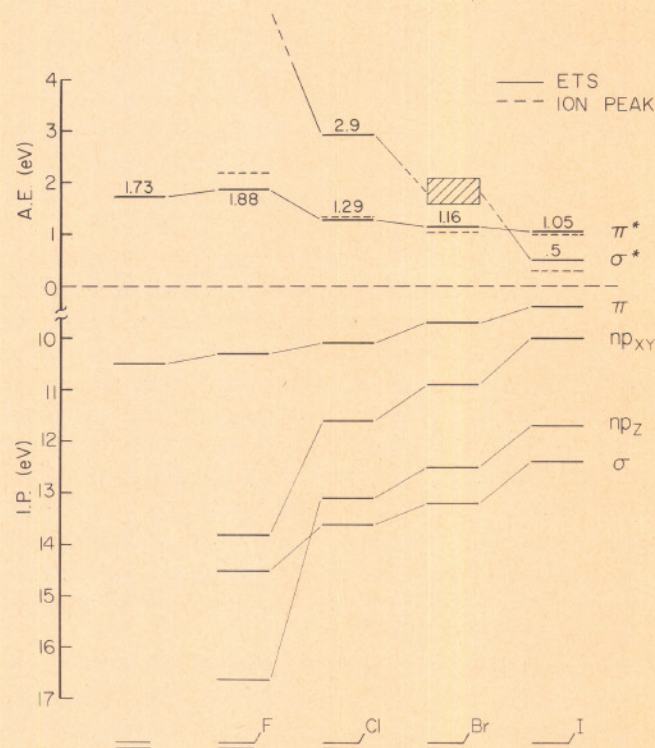


FIG. 2. Correlation diagram giving the attachment energies (AE) and vertical ionization potentials (I.P.) for the vinyl halides. The positions of the energy maxima for dissociative attachment are shown as dashed bars. The uncertainty in AE's is ± 0.01 eV for measurements given to one decimal place and ± 0.05 eV for measurements given to two places. The I.P.'s are from Ref. 10.

tributable to a resonance interaction¹¹ or to geometric changes induced by the fluorine.⁴ The effect is apparently not important for the halogens below the second row. Such an effect has been observed previously¹² and is presumably due to the fact that the spatial distribution of an np_z ($n \geq 3$) orbital is much different from the $C2p_z$ which is the primary component of the ethylenic π^* orbital. For vinyl chloride, bromide, and iodide, the π^* orbital is stabilized by the inductive effect¹¹ of the halogen substituent. The carbon-halogen σ^* is similarly stabilized. Note that for the anion states the stabilization increases on going down group VII in opposition to a decreasing electronegativity. The important property of the halogen in this case is not the electronegativity but rather the electron capacity of the halogen. The electron capacity increases with increasing atomic number.¹³

The ordering of anion states in vinyl iodide can not be unambiguously determined from the ETS data. However, the relatively slow rate of stabilization of π^* down the vinyl halide series, and the rapid rate of stabilization of σ^* evident in the correlation diagram, strongly imply that the σ^* orbital in vinyl halide lies below the π^* .

Dissociative attachment

The products of dissociative attachment to the vinyl halides are essentially always a vinyl radical and a halide ion. As is evident from comparing Fig. 3 to Fig. 1, detachment of the halide anion is always associated with the π^* electron capture resonance. In fact, with the exception of vinyl io-

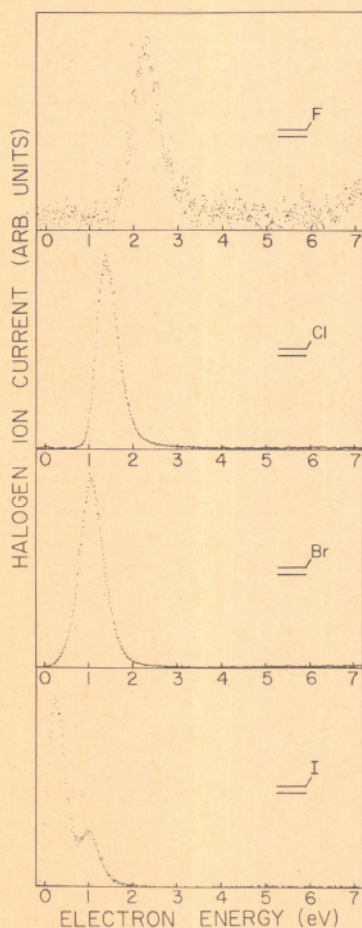


FIG. 3. Halide ion yield as a function of electron energy for dissociative attachment to the vinyl halides.

dide, dissociative attachment is uniquely associated with the π^* resonance for electron energies below 7 eV. The location of the ion production peaks and their association with the ETS data is indicated in the correlation diagram (Fig. 2). Interestingly, dissociative attachment to vinyl fluoride and vinyl chloride, molecules of great practical significance, has only recently been studied.^{8,14,15} These new results are in agreement with the present work.

In addition to the similarities of dissociative attachment in the various vinyl halides, there are a number of very interesting differences. These differences can most productively be discussed in terms of the relevant potential energy curves. Approximate potential curves can be constructed from the ETS data along with thermochemical and spectroscopic data for the dissociation fragments. As illustrated in Fig. 4, the position of the asymptote for the ground state vinyl halide curve is established by the carbon-halogen bond strength.¹⁶ The position of the limit for dissociation to a 1S halide ion and a $^2\Sigma$ ground state vinyl radical requires only the halide electron affinity.¹⁶ Since the vinyl halides do not have positive electron affinities, the ground state curve is expected to be repulsive. Because of the symmetry of the dissociation products this must be a $^2\Sigma$ surface of the vinyl halide anion. Above the asymptotic limit of the ground state curve lies the limit corresponding to a halide ion and the $^2\Pi$ vinyl radical. This is generally believed to correlate with the anion state giving rise to the prominent π^* resonance.⁹ This $^2\Pi$ anion curve is drawn so that the vertical distance above the minimum of the neutral ground state curve is equal to the observed energy of the π^* resonance. As pointed out by Clarke and Coulson¹⁷ and Burrow *et al.*,⁹ there is the possibility of a vinyl halide anion's dissociating to a vinyl anion and a halogen atom. The corresponding limit is established by the electron affinity of the vinyl radical which is believed to be positive and is estimated to be about 0.6 eV.^{9,18} This limit correlates with a $^2\Pi$ and two $^2\Sigma$ anion surfaces. Burrow *et al.*⁹ argue that the least repulsive of these, a $^2\Sigma$ anion state correlates with the σ^* resonance, hence this curve is drawn so that the vertical distance above the minimum of the neutral ground state curve is equal to the observed energy of the σ^* resonance.

In all the vinyl halides, dissociation following attachment of electrons of energy less than about 2.5 eV must proceed along the repulsive $^2\Sigma$ ground state surface. From symmetry considerations or, alternatively, on the basis of the conservation of orbital angular momentum, it is therefore surprising that dissociative attachment is associated with formation of the $^2\Pi$ anion state which correlates with the π^* ETS resonance.¹⁷ However, calculations for the fluoroethylene,¹⁹ as well as our calculations for vinyl chloride,²⁰ imply that the planar $^2\Pi$ anion is unstable with respect to distortion out of the plane. This distortion mixes Σ and Π states and allows the $^2\Pi$ anion access to the $^2\Sigma$ dissociation limit.

Heni and co-workers^{8,14} state that, in the fluoroethylenes, dissociative attachment does not generally lead to a fluoride ion and a vinyl radical. We find that the cross section for dissociative attachment to vinyl fluoride is relatively small and that fragmentation to $F^- + C_2H_3(^2\Sigma)$ is essentially the only dissociative channel. Furthermore, unlike all oth-

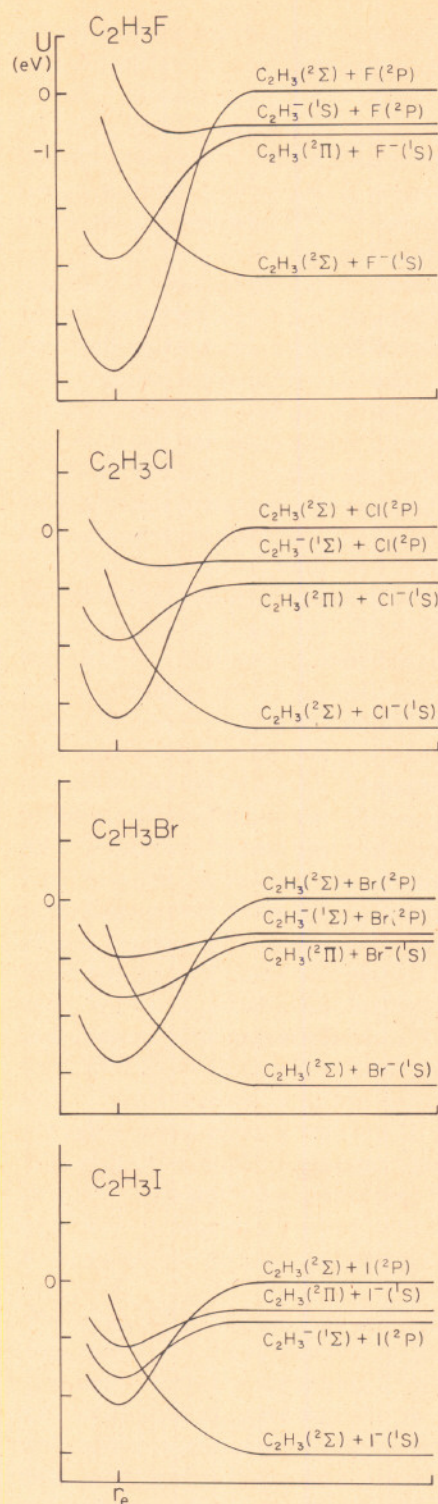


FIG. 4. Approximate potential energy vs carbon-halogen distance for the ground state of the vinyl halides and low-lying states of the anions.

er cases discussed here, the peak in the dissociative attachment cross section lies well above the energy of the π^* electron scattering resonance. The reason both for this shift and the small cross section is evident from the potential energy curves since, unlike the other vinyl halides, the dissociative $^2\Sigma$ anion curve must cross the $^2\Pi$ curve at an energy well above the Franck-Condon region for electron capture.

In vinyl chloride the dissociative attachment peak is congruent with the π^* resonance in the elastic electron scattering spectrum. There is no dissociative attachment proceeding through the σ^* resonance although the potential curves suggest that the $^2\Sigma$ anion state going to $C_2H_3^- + Cl(^2P)$ is weakly bound at best. Furthermore, this $^2\Sigma$ state lies in the continuum above the $^2\Sigma$ ground state which is surely dissociative.²¹ The failure to dissociate may be a result of a very short lifetime of the σ^* resonant state or a misplacement of the $C_2H_3^- + Cl(^2P)$ limit.

The single electron transmission resonance in vinyl bromide is broad and asymmetric. The fragmentation spectrum has a single narrow peak located at the energy of the leading edge of the peak in the electron transmission spectrum. An obvious interpretation is that the peak in the electron transmission spectrum includes both the π^* and σ^* resonance and, as suggested in the correlation diagram in Fig. 2, the σ^* resonance is to the high energy side of the π^* resonance.

The correlation diagram indicates that the σ^* resonant state stabilizes much more rapidly than the π^* state with increasing atomic weight of the halogen substituent in the vinyl halides. This relative stability of the π^* resonant state suggests the change in ordering of states in vinyl iodide indicated in Figs. 2 and 4. Electron capture into both σ^* and π^* states of vinyl iodide results in dissociation to an iodide anion and a vinyl radical. This is not surprising since the σ^* resonant state in vinyl iodide is quite low in energy and can be expected to be relatively long-lived, thus enhancing the probability of coupling with the dissociative $^2\Sigma$ ground state of the anion.

CHLOROETHYLENES

Burrow and co-workers have published electron transmission spectra of all the chloroethylenes.⁹ Presentation of the spectra obtained in the present work was deemed unnecessary as they are essentially identical to the previous results. The electron transmission data along with photoelectron spectroscopic measurements²² of the valence ionization potentials are presented as a correlation diagram in Fig. 5. The

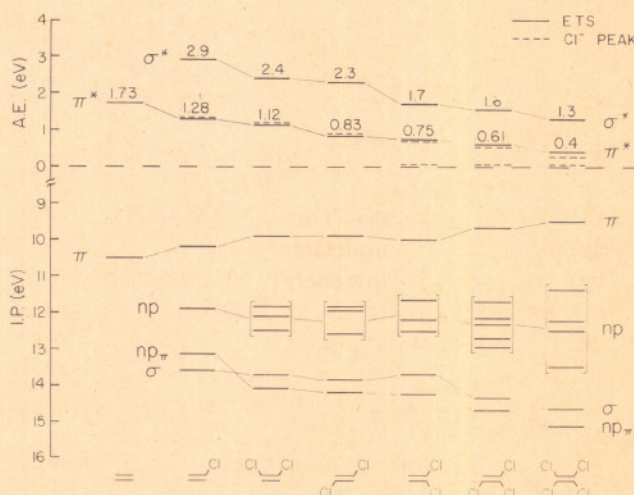


FIG. 5. Correlation diagram giving the attachment energies (A.E.) and ionization potentials (I.P.) for the chloroethylenes. The I.P.'s are from Ref. 22. The energies for chloride detachment are also indicated.

assignment of transmission resonances to electron capture into π^* and σ^* orbitals is strongly supported by the work of Burrow *et al.*⁹ The dominance of inductive stabilization upon the unfilled orbitals is evident from the decrease in both σ^* and π^* attachment energies with increasing number of chlorines. For the filled π orbital the inductive effect is offset by a resonance interaction with the chlorine $3p_z$. This resonance or mesomeric effect is more important for the filled orbitals because the difference in energy between the π molecular orbital and the chlorine $3p_z$ orbital is small. It is noteworthy that for all except C_2Cl_4 , only a singly broad σ^* resonance appears. From symmetry considerations one would predict a multiplicity of low-lying σ^* orbitals corresponding to the various combinations of (ideally) localized σ^* C-Cl bonds. In C_2Cl_4 a second broad σ^* resonance appears at 5.4 eV. The significantly greater inductive stabilization associated with 1,1-chlorosubstitution as opposed to the 1,2-substitution is also worthy of note. Apparently the strict additivity of the stabilizing effect of halogen substituents holds only for substituents which cannot interact.

The chloride ion is far and away the major ion arising from low energy electron attachment to the chloroethylenes. This phenomenon has been observed in all the chloroethylenes except for vinyl chloride by Johnson, Christophorou, and Carter²³ using a low resolution ($\Delta E = 250$ meV) electron beam method. In their measurements the energy scale appears to be shifted by about 0.2 eV relative to the present measurements. Dissociative attachment to trichloroethylene was investigated in a swarm experiment by Christophorou and co-workers²⁴⁻²⁶ and in an electron beam experiment ($\Delta E = 90$ meV) by Illenberger *et al.*^{15,27} The results of the present high resolution measurement are shown in Fig. 6. As indicated in the correlation diagram of Fig. 5, dissociative attachment is associated with the π^* resonance in the electron scattering cross section. In addition it can be seen that, as the π^* resonance approaches 0 eV in the heavier members of the series, an abrupt enhancement of the dissociative attachment cross section occurs at threshold. This threshold does not appear in Illenberger's spectra.¹⁵ A low energy enhancement does appear in Johnson's results²³ but does not occur precisely at 0 eV. This is presumably a result of earlier apparatus' inability to produce current from threshold upwards.

An explanation for the enhancement of dissociative attachment at low energies has been put forward by O'Malley²⁸ and Illenberger.²⁷ Simply put, the effect derives from the dependence of the lifetime of a temporary anion upon the inverse of the electron energy. This allows dissociation to effectively complete with autodetachment when an anion is formed by capture of a very low energy electron. What is not apparent is how a transition is possible when even in C_2Cl_4 the $^2\Pi$ anion state lies a few tenths of an eV vertically above the neutral ground state. The answer lies in a consideration of the out-of-plane relaxation of the $^2\Pi$ anion (*vide supra*). The potential energy curves as a function of the out-of-plane distortion angle for the neutral ground state and $^2\Pi$ anion state are illustrated schematically in Fig. 7. It can be seen that while the vertical transition from the middle of the ground state potential well may require a few tenths of an eV,

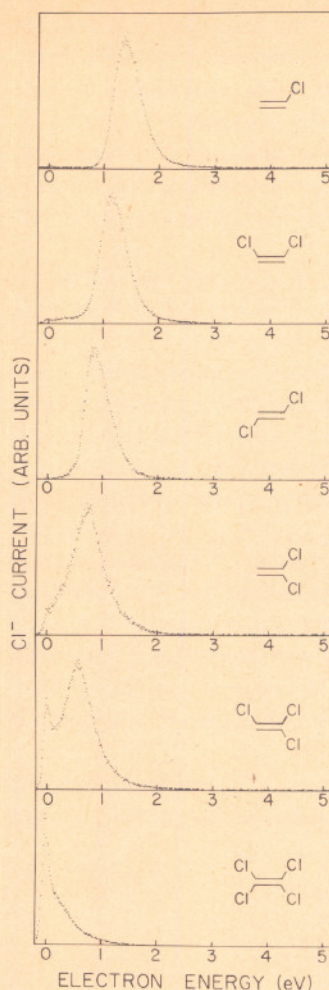


FIG. 6. Halide ion yield as a function of electron energy for dissociative attachment to the chloroethylenes.

there is the possibility of Franck-Condon overlap for a 0 eV transition.

HALOBENZENES

The low-lying unoccupied orbitals of benzenes are antibonding π orbitals designated π_4^* , π_5^* , and π_6^* . In benzene the first pair (π_4^* , π_5^*) are degenerate. Monosubstitution on benzene lifts this degeneracy. With respect to a single substituent, one member of the π_4^* , π_5^* pair is symmetric (*S*) and the other antisymmetric (*A*). Only one of these, $\pi^*(S)$, can interact in a resonance fashion with substituent orbitals of p_z symmetry. In the last decade negative ion resonant states

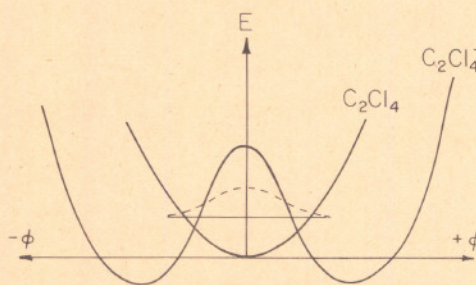


FIG. 7. Approximate representation of potential energy vs out-of-plane distortion angle for the neutral ground state and $^2\Pi$ anion state of tetrachloroethylene.

involving electron capture into the benzene π^* orbitals of various halobenzenes have been observed in electron transmission spectra.²⁹⁻³¹ Before this, evidence for some of these anion states was obtained in trapped electron³² and threshold electron³³ experiments. In addition to π^* resonances, one can anticipate a σ^* resonance associated with a predominantly carbon-halogen σ^* orbital analogous to the σ^* orbital in the vinyl halides.

Electron transmission spectra of benzene and all the halobenzenes are shown in Fig. 8. ETS and PES^{22,34} data are assembled as a correlation diagram in Fig. 9. The dominating inductive stabilization of the unoccupied orbitals is immediately evident. It is noteworthy that the stabilizing effect of the substituents F to I increases in opposition to a decreasing electronegativity of the elements F to I. As noted previously the inductive effect of halogen substituents increases with increasing electronic charge capacity, not with increasing electronegativity. The anticipated σ^* resonance is only apparent in the spectrum of chlorobenzene. For fluorobenzene this resonance can be expected to be high in energy and very broad. In bromobenzene the σ^* resonance merges with the π_4^*, π_5^* resonances and in iodobenzene it is evident from the dissociative attachment data that the σ^* resonance is below the π_4^*, π_5^* resonances.

The obvious splitting of the π_4^*, π_5^* pair in fluorobenzene is evidence for a destabilizing resonance interaction between

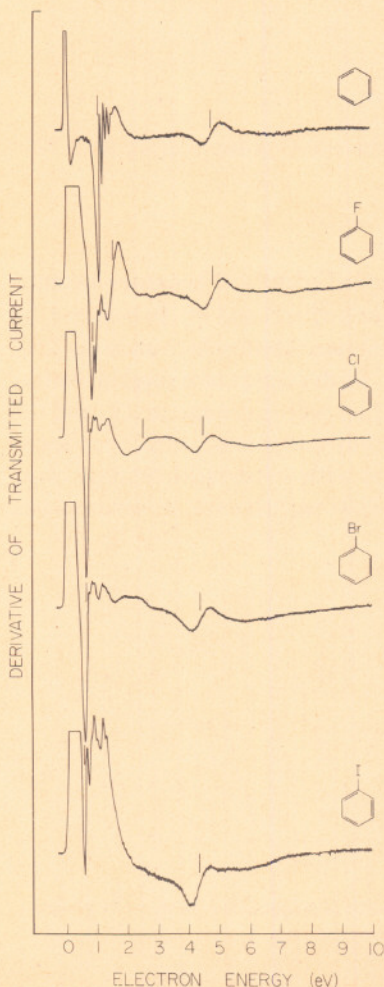


FIG. 8. Derivative electron transmission spectra of benzene and the halobenzenes.

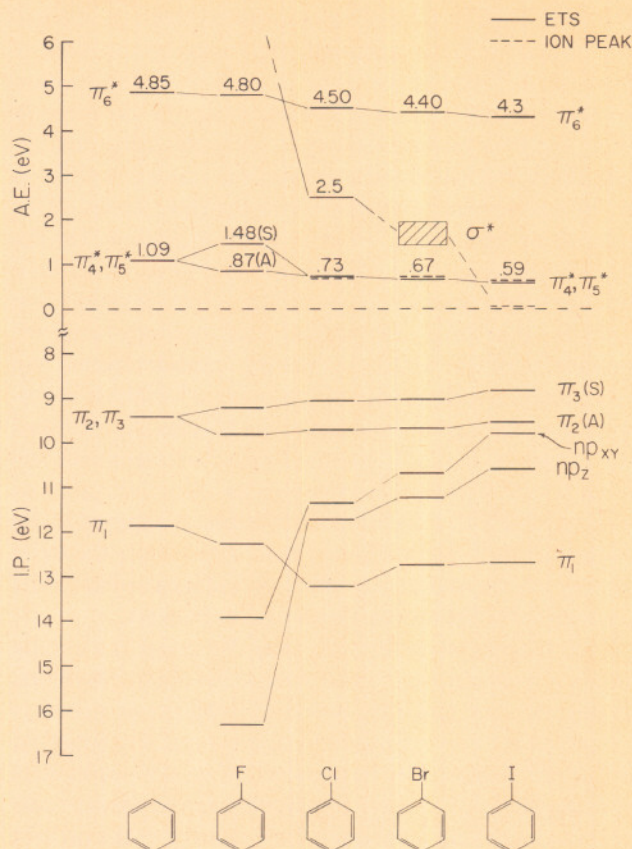


FIG. 9. Correlation diagram giving the attachment energies (AE) and ionization potentials (I.P.) for the halobenzenes. The I.P.'s are from Refs. 22 and 34.

the symmetric member of this pair, $\pi^*(S)$, and the occupied $F2p_z$. The antisymmetric member of this pair, $\pi^*(A)$, is unaffected by the resonance interaction but is stabilized by the inductive effect. As noted for the case of vinyl fluoride, the π^*-np_z resonance interaction is only significant between atoms from the same row of the periodic table.

Dissociation of a halide ion upon capture of a low energy electron has been observed by Wentworth and co-workers in thermal electron attachment to chloro-, bromo-, and iodobenzene^{35,36}; by Christophorou *et al.*, for chloro-, bromo-, and iodobenzene in a low resolution swarm-beam experiment³⁷; and by Stockdale and Hurst for chloro- and bromobenzene in a swarm experiment.³⁸ The thermodynamic threshold for dissociative attachment to fluorobenzene is about 1.63 eV, hence low-energy resonant dissociative attachment to fluorobenzene is not expected nor is it observed. High resolution dissociative attachment spectra from the present work are presented in Fig. 10. It is immediately obvious that dissociation is associated with the π^* electron capture resonance observed in the electron transmission spectrum. As in the case of the vinyl halides, this process must proceed as a result of an out-of-plane excursion of the halogen atom which permits mixing of the $^2\Pi$ anion state with the repulsive $^2\Sigma$ ground state leading to $C_6H_5(X^2A_1) + X^-$. The out-of-plane geometry must not be particularly stable since bromobenzene does not display a threshold enhancement such as is seen in trichloro- and tetrachloroethylene. The dissociation near 0 eV in iodobenzene is attributed to the

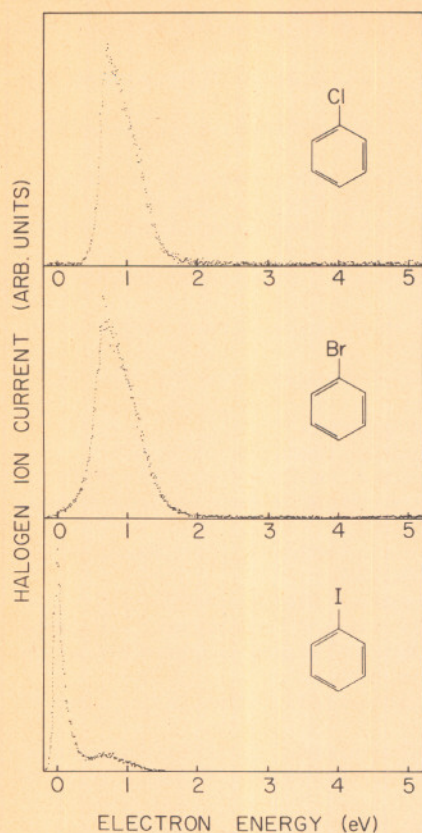


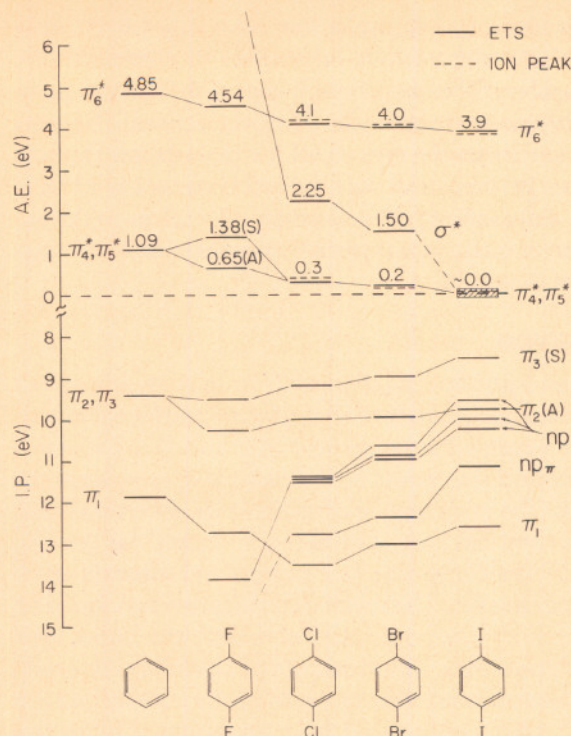
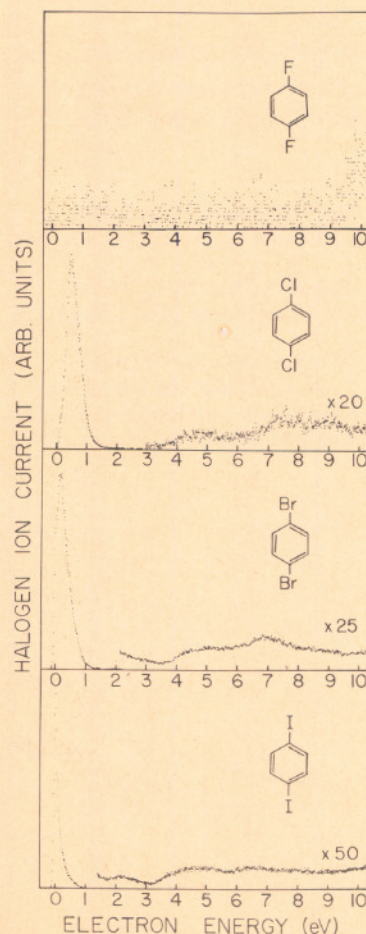
FIG. 10. Halide ion yield for dissociative attachment to the halobenzenes.

σ^* electron capture resonance where, presumably, low energy and corresponding long lifetime favor the dissociation channel over autodetachment.

PARA-DIHALOBENZENES

1,4-disubstituted benzenes are of course more symmetrical than monosubstituted benzenes. They offer the possibility of observing the interaction of localized carbon-halogen σ systems and permit the investigation of additive substituent effects. High resolution spectra of all the *para*-dihalobenzenes save *para*-diiodobenzene have been published.^{31,39} ETS data from the present work along with PES data^{34,40} are assembled as a correlation diagram in Fig. 11. The dominance of the inductive effect of the halogens substituents upon the anion state energies is immediately obvious. A comparison of the π^* resonance energies for the disubstituted benzenes (Fig. 11) with those for the monosubstituted benzenes (Fig. 9) reveals that the stabilizing effect of halogen substituents is roughly additive. For example π_6^* in chlorobenzene is stabilized by about 0.4 eV relative to benzene while π_6^* in 1,4-dichlorobenzene is about 0.8 eV lower than the benzene. The π_4^*, π_5^* pair is stabilized by 0.4 eV in chlorobenzene and by 0.8 eV in 1,4-dichlorobenzene. The presence of two relatively localized carbon-halogen σ systems should give rise to two σ^* resonances; however, only a single σ^* resonance similar to that in the halobenzenes is observed, hence the splitting must be of the order of 0.5 eV or less.

Finally the dissociative attachment spectra are shown in Fig. 12. As for the case of fluorobenzene, dissociation of

FIG. 11. Correlation diagram giving the attachment energies (AE) and ionization potentials (I.P.) for the *para*-dihalobenzenes. The I.P.'s are from Refs. 34 and 40.FIG. 12. Halide ion yield for dissociative attachment to the *para*-dihalobenzenes.

difluorobenzene by capture of low energy (< 1.6 eV) electrons is thermodynamically impossible. In *para*-dichloro-, and *para*-dibromobenzene, detachment of the halogen anion is primarily associated with the π_4^*, π_5^* resonances. The cross sections are obviously very small for dissociation through higher energy resonances. In 1,4-diiodobenzene the σ^* resonance as well as the π_4^*, π_5^* resonances all lie close to threshold, the cross section for dissociative attachment is only significant at threshold.

CONCLUSION

A systematic investigation of electron attachment and dissociative attachment to the haloalkenes and halobenzenes has made possible the assignment of Σ and Π anion states whose identification would not be possible from isolated observations. The investigation of compounds, wherein a halogen substituent has been systematically varied, has demonstrated the stabilizing effect of halogen substituents upon anion state energies. The relative stabilization was found to depend upon the charge capacity of the halogen rather than the electronegativity. Resonance effects involving the quantum mechanical interaction of the halogen p_z orbital and the alkene π^* orbital were found to be important only for the second row halogen, fluorine. In some of the halogenated alkenes, a remarkable enhancement of the cross section for dissociative attachment of threshold energy electrons has been observed. This is not a general phenomenon and the source of this enhancement cannot be said to be understood.

ACKNOWLEDGMENTS

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