Conclusion

In short, charge-transfer transitions occurring in the anionic forms of malonic esters of heteroaromatic and aromatic compounds are manifested as spectral changes in two wavelength regions (Table I). In the 240–260-nm region, new, intense peaks or general hyperchromism are evident in intramolecular charge transfer or $C\pi \rightarrow \pi^*$ transitions, while in the long wavelength end (above 270 nm) of the spectra, absorption shoulders with $\epsilon < 700$ or general broadening are often observed. In general, compounds with the donor and the acceptor moieties directly attached to one another show little effect in the long wavelength region. However, new, intense absorption bands are conspicuous. Compounds with various bridges show some degree of hyperchromism in the shorter wavelength region and absorption shoulders in the long wavelength region. These effects decrease with increasing separation between the two moieties. Very little effect can be observed with benzamido derivatives, where the separation by -CONH- is somewhat less than that by the $-CH_2CH_2-$ bridge. This evidence suggests that heteroatoms exert certain subtle influences, the effects of which become quite pronounced as in the cases of compounds with a nitrogen bridge. Also, the electron-withdrawing NO_2 groups on phenyl rings increase the capability of the acceptor to accept the electron; the result is stronger interaction with the donor moiety. Thus, the intensities of the charge-transfer bands increase accordingly.

Experimental Section

Ultraviolet Spectra. Ultraviolet absorption spectra were recorded on a Cary recording spectrophotometer, Model 14, at ambient temperature. Malonic ester derivatives of heterocyclic and carbocyclic compounds were measured in pH ≤ 4 buffered aqueous solutions and the spectra of their anionic forms were determined in pH 12 buffered aqueous solutions. Those of the water-insoluble compounds were obtained in absolute ethanol and 0.01 *M* NaOH in absolute ethanol, respectively.

Syntheses. Diethyl uracil-1-malonate and diethyl *N*-methylanilinomalonate were prepared using the methods reported earlier.[1a]

Diethyl 2,4-dinitroanilinomalonate was synthesized according to the method of Harnik and Margoliash,[18] mp 103° (lit. 102.5–103.5°).

Diethyl phenoxymalonate was prepared by mixing sodium phenoxide (0.1 *M*, 11.6 g) and diethyl bromomalonate (0.1 *M*, 26.3 g) in a flask equipped with a thermometer and a reflux condenser bearing a $CaCl_2$ tube. Vigorous reaction occurred and the temperature rose to 120°. Upon completion of the reaction the temperature dropped to 60°. The reaction mixture was kept at 80° for 1 hr. After the mixture was cooled, the product was extracted several times with anhydrous ether. The ether was removed from the combined extracts and the residue was then subjected to fractional distillation. The fraction distilled at 130–170° (5 mm) was collected. Redistillation of this fraction gave 11 g of material with bp 147–150° (5 mm). *Anal.* Calcd for $C_{13}H_{16}O_5$: C, 61.90; H, 6.31. Found: C, 62.03; H, 6.25; mol wt, *m/e* 252 (mass spectrum).

Diethyl *p*-nitrophenoxymalonate was synthesized by the reaction of equimolar amounts of sodium *p*-nitrophenoxide and diethyl bromomalonate in dimethylformamide using a procedure described for diethyl uracil-1-malonate. The crude product (~80%) was purified by crystallization in absolute ethanol to constant mp 63–64°. *Anal.* Calcd for $C_{13}H_{15}O_7N$: C, 52.52; H, 5.05; N, 4.71. Found: C, 52.48; H, 5.00; N, 4.67; mol wt, *m/e* 297 (mass spectrum).

Diethyl phenylmalonate, diethyl benzylmalonate, and diethyl 2-phenethylmalonate, obtained from Aldrich Chemical Co., were redistilled and only the middle fractions boiling at 170–171° (14 mm),[19] 162–163° (10 mm),[19] and 180–181° (16 mm),[20] respectively, were used for the spectral determinations.

Diethyl benzamidomalonate, obtained from Chemical Procurement Lab. Inc., was recrystallized to constant mp 61–62° (lit.[19] 61°).

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Halogen Atom Charge-Transfer Complexes in the Vapor Phase

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Abstract: Transient absorption has been detected following the flash photodissociation of iodine in benzene, cyclohexane, methyl iodide, ethyl iodide, methyl bromide, ethyl bromide, methyl chloride, and ethyl chloride and similarly with bromine in the same alkyl bromides and chlorides and in xenon. The correlation between the spectral band maxima and the ionization potentials of the donor species clearly indicate the charge-transfer character of these spectra. The bands are blue shifted from those of the comparable liquid-phase species, although the interaction energies appear to be about the same. The data do not distinguish between complex and collisional or contact charge transfer between the iodine or bromine atoms and the various donor species, but in combination with vapor-phase third-order atom recombination rates the results are consistent with predominantly complex interactions.

Many studies have recently been reported on vapor-phase molecular iodine charge-transfer (CT) complexes.[1–10] In general, the absorption maximum of the CT band shifts to the blue, the formation constant (*K*) increases, and the extinction coefficient (ϵ) de-

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Table I. Transient Vapor Phase Absorption Spectra

Donor	$[I_2]$, mol/l.	$[Br_2]$, mol/l.	P_{Donor}, atm	Temp, °C	Analyzing filter	$\lambda_{\max}$, nm
Benzene	8.2×10^{-5}		1.0	92	*a*	430
Cyclohexane	6.1×10^{-5}		1.0	87	*b*	310
Ethyl iodide	5.5×10^{-5}		1.0	82	*a*	425, 360
Methyl iodide	3.0×10^{-5}		1.0	50	*b*	416, 350
Ethyl bromide	1.0×10^{-5}		0.42	Room	*c*	323
		1.5×10^{-4}	0.32	Room	*a, d*	345
Methyl bromide	0.9×10^{-5}		0.92	Room	*e*	313
		1.8×10^{-4}	0.43	Room	*a, d*	335
Ethyl chloride	0.3×10^{-5}		1.0	Room	*f*	279
		2.5×10^{-4}	0.86	Room	*d*	310
Methyl chloride	1.1×10^{-5}		2.1	Room	*f*	268
		1.7×10^{-4}	0.42	Room	*d*	300
Xenon		2×10^{-4}	4.0	Room	*c*	257

[a] Plate glass. [b] Pyrex. [c] Quartz. [d] Bromine (10^{-2} *M*) in carbon tetrachloride, 1-cm light path. [e] 50 g of $NiSO_4 \cdot 6H_2O$ + 12 g of $CoSO_4 \cdot 7H_2O$ in 100 ml of solution (5 vol % acetone, 95 vol % water), 1-cm light path. [f] 1 g of $CaSO_4 \cdot 5H_2O$ + 63.8 g of $NiSO_4 \cdot 6H_2O$ in 200 ml of H_2O, 1-cm light path.

creases in going from the liquid to the vapor phase for weak complexes but not necessarily for the stronger interactions.[9]

CT complexes between halogen atoms and a wide variety of solvents have been detected in the liquid phase by their transient CT absorption following flash photolysis of the molecular halogen[11-16] or solvent pulse radiolysis.[17-21] However, although such complexes are assumed to be intermediates in general mechanisms for halogen atom gas-phase recombination processes,[22] very few complexes have actually been directly observed in the gas phase by spectral means. The unstable molecule NOI has been detected ($\lambda_{\max}$ *ca.* 430 nm) in the recombination of iodine atoms in the presence of NO (a very efficient third-body chaperon),[23] and very weak gas-phase absorption was observed between 420 and 430 nm following flash photolysis of molecular iodine in methyl iodide[12] (although nothing was observed under similar conditions for I_2 in ethyl iodide, ethanol, or benzene). We report here a study of the spectral characteristics of iodine and bromine atom complexes with a variety of π- and n-donor species in the vapor phase.

Experimental Section

The flash spectrophotometer was of conventional design as described previously[24] but without the polarizer and analyzer quartz prisms. Maximum flash energy was 5000 J; peak intensity was reached in 7 μsec, with a half-width *ca.* 11 μsec at 500 nm. For cells containing iodine, the flash light was filtered through 10 mm of saturated uranyl nitrate solution; for bromine systems, a filter solution consisting of 64 g of uranyl nitrate per 200 ml of water was used. The continuous analyzing light from the dc-stabilized Osram XBO-450 xenon arc was also filtered with the appropriate liquid or solid filter, specified below, to prevent direct photolysis of the reactants in the cases of observed irreversible processes. Transient changes in absorbance were obtained point by point from voltage-time oscillograms taken approximately every 10 nm (bandwidth determined by the entrance slit of the Zeiss MM12 monochromator to be *ca.* 2 nm) at a constant time after initiation of the flash (usually 75 μsec, at which time the flash light intensity had decayed to a negligible value but only limited halogen atom recombination had occurred).

The reaction cells (Pyrex or quartz, depending on the system) for use at ambient temperature were cylindrical, 25 mm o.d. and 100-mm light path, with optically flat fused windows. For runs at elevated temperatures similar cylindrical cells were constructed with 20-mm evacuated chambers added at each end and surrounded (to within 10 mm of each end) by a 10-mm annular jacket through which water was circulated from a constant-temperature bath. All liquid donor species were distilled and passed through a phosphorus pentoxide drying tube under vacuum before storage and use. Two different procedures were used for filling cells. For those cells involving donors that are vapors at room temperature and 1 atm pressure (and were to be studied only at room temperature), the desired pressure (corrected for the small change in volume between the isolating stopcock and point of sealing off) of the outgassed vapor was admitted into the evacuated cell and frozen out, a measured amount of iodine or bromine vapor was transferred to the cell from a calibrated metering chamber and also condensed, and the cell was sealed off from the vacuum transfer apparatus. In other cases involving room temperature liquid donors, a measured amount of the liquid was outgassed, dried under vacuum by passage through the phosphorus pentoxide tube, and frozen out in the reaction cell; the halogen was added and the cell removed from the vacuum transfer apparatus as above.

Results

Transient absorbing species in the vapor phase have been observed spectrally following flash photodissociation of iodine or bromine in a variety of CT donors. Spectral maxima are given in the last column of Table I for all added gases studied (except for toluene and diethyl sulfide), and these maxima, expressed as $hc/\lambda_{\max}$,

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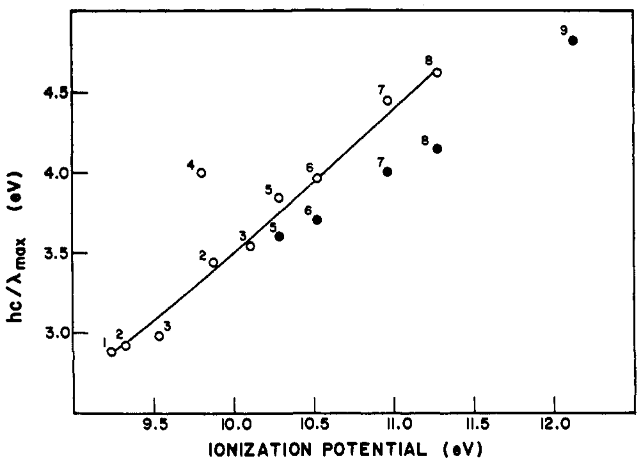

Figure 1. Dependence of the absorption maximum upon the ionization potential of the donor species: open circles, iodine; closed circles, bromine. (1) benzene; (2) ethyl iodide; (3) methyl iodide; (4) cyclohexane; (5) ethyl bromide; (6) methyl bromide; (7) ethyl chloride; (8) methyl chloride; (9) xenon.

are plotted in Figure 1 as a function of the ionization potential I_D of the donor species. Toluene and diethyl sulfide gave transient absorbances in the visible spectral region with iodine; however, the toluene maximum (*ca.* 460 nm) was obscured in the overlapping molecular iodine band which led to a net decrease in absorbance in this region because of molecular iodine dissociation. The diethyl sulfide results are of uncertain value because of apparent condensation or irreversible reactions occurring at the reaction cell surface. The presence of transient absorbance characteristic of neither species alone and the relationship between the energies of the maximum absorption and ionization potentials of the added gases shown in Figure 1 clearly indicate that these are charge-transfer spectra.

Two maxima are observed in the spectra of the iodine atom–methyl iodide and iodine atom–ethyl iodide species (Table I), each of the separate bands being well defined and of relatively small half-bandwidth (*ca.* 2200 cm^{-1}) in comparison with most CT bands. Multiple CT bands are observed with molecular iodine in a variety of systems in the liquid or vapor phase,[25] with atomic iodine in the liquid phase with *p*-xylene,[11] and with ethyl iodide (by flash photolysis[12] but not by pulse radiolysis[21]). Primarily these are interpreted as transitions from more than one energy level of the donor species, in the case of *p*-xylene the two levels resulting from the removal of the twofold degeneracy of the e_{1g} orbital of benzene.[26] The observed energy differences between the multiple bands given in Table I are very close to the differences between the first and second ionization potentials of the alkyl iodides (9.49 and 10.11 eV for methyl iodide[27] and 9.30 and 9.88 eV for ethyl iodide[28]) and therefore are assigned to these two transitions. The four bands for the two alkyl iodide complexes are shown at these four ionization potentials in Figure 1. Similar effects should also be present for the alkyl bromide and chloride complexes. However, the difference between the first two ionization potentials decreases with decreasing halogen atomic weight[28] for alkyl halides (although the ionization potentials increase) making resolution of the two bands more difficult, and this and the overlapping donor molecule absorption bands in the same uv spectral region as the CT bands have prevented detection of two separate CT bands in alkyl bromide and chloride systems.

It is evident that an (approximately) linear relationship between the energy of the absorption band and the ionization potential of the donor species, with slope less than unity, results for each set of acceptor (I or Br atom) species independent of the nature of the donor. This linear behavior and small slope is observed for a variety of sets of donors and a given acceptor and is typical of charge-transfer interactions over a limited range of ionization potentials and for a comparable series or type of donors.[29] However, there is no theoretical basis for this linearity, and various other approximate correlations have been presented including the parabolic equation for weak complexes[30]

$$h\nu_{CT} = hc/\lambda_{max} = I_D - C_1 + C_2/(I_D - C_1) \qquad (1)$$

On this basis, the best values for the parameters in eq 1 for iodine atoms (solid line on Figure 1) are $C_1 = 6.9$ eV and $C_2 = 1.2$ eV.^{2} The data for bromine atoms are too limited to justify even approximate curve fitting to eq 1, but the observed trend to lower values for $h\nu_{CT}$ in all cases in going from iodine to bromine (same donor) is consistent with the higher electron affinity of the bromine atom ($E_A = 3.1$ and 3.6 eV for iodine and bromine atoms, respectively)[31] if $C_1 = E_A + C_1'$.

Rao and coworkers[9] have recently shown that, for a series of weak molecular iodine complexes with π and n (other than amine) donors demonstrating a comparable relationship between $h\nu_{CT}$ and I_D in the liquid phase, the value for C_2 in the vapor phase (3.9 eV^2) is greater than that in the liquid phase (2.8 eV^2), indicating greater vapor-phase stability. For stronger interactions, however, a more appropriate equation based on the variation method is[32]

$$(h\nu_{CT})^2 = [(I_D - C_1)/(1 - S_{01}^2)]^2 \times [1 + 4\beta_1\beta_0/(I_D - C_1)^2] \qquad (2)$$

where S_{01} is the overlap integral, and β_0 and β_1 are the resonance integrals $(H_{01} - S_{01}W_0)$ and $(H_{01} - S_{01}W_1)$, respectively. Thus, β_0 is related to energy of the pure "no bond" state, W_0. The best fit of the data in Table I to eq 2 for iodine atoms, using the method and graph of Mulliken and Person,[33] gives $\beta_0 = -1.0$ eV, $S_{01} = 0.3$, and $C_1 = 8.1$ eV. These parameters are essentially identical with those for comparable iodine atom CT complexes in the liquid phase[12] even though the actual CT absorption maxima are strongly blue shifted in going from liquid to vapor phase. On this basis the interaction energies are comparable in the two phases for the iodine atom complexes as also observed for the strong molecular iodine–amine complexes,[9] in contrast to the behavior of the weaker molecular iodine–π donor

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species[1]. Admittedly, however, this correspondence of parameters is with very large error limits, and it is doubtful that this method should be used to infer the strengths of these vapor-phase complexes.

For two of the donors, benzene and cyclohexane, the data are now available with this work to compare both the molecular and atomic iodine CT spectra in liquid and vapor phases (Table II). Although the differences for the benzene CT spectra are larger than those for cyclohexane, it is apparent that there are no major differences among the four systems, suggesting similar weak or "contact" interactions in all cases. Solvent effects may become more apparent when it is possible to compare the stronger iodine–diethyl sulfide complexes in the gas and liquid phases. However, the differences in spectra represented by $\Delta h\nu_{CT}$ are quite sensitive to the particular values for λ_{max} chosen and therefore subject to considerable error in view of the broad, structureless CT bands obtained in both phases and the specific solvent effects observed. Indeed, Tamres and Grundnes have recently reported results also on the cyclohexane–molecular iodine system,[10] in which no CT absorption maximum is obtained unless a specific hydrocarbon pressure broadening of the far-uv iodine spectrum is assumed. Choosing *n*-pentane as a reference system, λ_{max} for cyclohexane-I_2 is 215 nm, giving $\Delta h\nu_{CT}$ = 0.65 eV between the liquid and vapor-phase spectra.

Table II. Comparison of I_2 and I Charge-Transfer Spectra

	Benzene			Cyclohexane		
Acceptor	λ_{max}, nm (liquid)	λ_{max}, nm (vapor)	$\Delta h\nu_{CT}$, eV	λ_{max}, nm (liquid)	λ_{max}, nm (vapor)	$\Delta h\nu_{CT}$, eV
I_2	292[a]	268[b]	0.38	242[c]	230[d]	0.27
I	495[e]	430	0.37	330[f]	310	0.24

[a] Reference 30, p 32. [b] Reference 1. [c] S. H. Hastings, J. L. Franklin, J. C. Schiller, and F. A. Matsen, *J. Amer. Chem. Soc.*, **75**, 2900 (1953). [d] Reference 9. [e] Reference 11. [f] Reference 17.

The bromine–xenon system is particularly interesting because it represents one of the highest donor ionization potentials for which CT absorption has been observed, but even in this case the CT spectrum is well within the spectral region to be expected from the behavior of the other bromine atom complexes. The interaction between a bromine atom and xenon would be expected to be weak, and comparable spectra involving molecular iodine in the vapor phase are generally considered to be predominantly contact charge transfer.[10] However, it is estimated[34] that the interaction potential between bromine and kyrpton atoms is 2 kcal/mol or several times larger than between two Kr atoms (Kr being the nearest neighbor to Br), and xenon is a more effective third body in vapor-phase iodine atom recombination than the other rare gases.[35] It has been estimated[36] from the trimolecular recombination rate constant, assuming a radical–molecule complex mechanism, that the formation constant for the XeI complex is *ca.* 5.4 l./mol. Assuming the same formation constant for the XeBr complex (a lower limit on the basis of relative electron affinities only) gives approximately 46% of the bromine atoms complexed under the conditions of this work and ϵ_c = 170 l. mol^{-1} cm^{-1} at 257 nm. This is essentially identical with the extinction coefficient for the very strong NOI complex[23] (228 l. mol^{-1} cm^{-1} at 430 nm) measured under conditions of high NO pressure and essentially 100% iodine atom complexation. It is thus possible that all of the spectra observed in this work are complex charge transfer rather than contact or collisional interactions, although further extinction coeffiicient, force constant, and formation constants measurements [particularly the cyclohexane system, which deviates in spectral behavior from all other donors studied (Figure 1)] are needed in order to clarify the source of the CT spectral band.

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