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Molecular Compounds and Their Spectra. XXI. Some General Considerations[1a]

Robert S. Mulliken[1b] and Willis B. Person[1c]

Contribution from the Laboratory of Molecular Structure and Spectra, Department of Physics, University of Chicago, Chicago, Illinois 60637, and Department of Chemistry, University of Florida, Gainesville, Florida 32601.

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Abstract: The question of the meaning and relative importance of classical electrostatic (Coulomb and polarization) and CT (charge-transfer) forces for the stability and dipole moments of EDA (electron *d*onor–*a*cceptor) complexes is critically examined and discussed in some detail for π–π and π–halogen complexes. The importance of distinguishing between complexes with donor and acceptor both sacrificial, which are usually weak, and complexes with increvalent (lone-pair) donors, which are often strong, is emphasized. It is concluded that, while classical electrostatic forces make significant contributions to the stability of donor–acceptor complexes, they are of predominant importance perhaps only for the weakest complexes. With reference to the role of London dispersion forces, it is pointed out that although these necessarily contribute to the stability of vapor-state complexes, their effects are approximately cancelled out in the formation of complexes in solution.

A moot question in the understanding of the structure and spectra of EDA complexes is the extent to which classical electrostatic forces, as against CT forces, contribute to the energy of formation and dipole moments of EDA complexes.[2–6] This question which we examine in more detail below, is difficult to resolve quantitatively because both kinds of force are often qualitatively expected to contribute to these properties. Briegleb earlier accounted for the stability of certain π–π complexes, in particular nitro-compound complexes, by electrostatic forces, but later[7] adopted Mulliken's view that CT forces are of predominant importance except in hydrogen-bonded complexes. However, Mulliken now agrees that electrostatic forces may be responsible to an important and very likely sometimes predominant (although not exclusive) extent for π–π and other relatively weak complexes, as well as for H-bonded complexes, whereas for strong n–σ and n–v complexes, CT forces are clearly predominant.[8] For this reason he has adopted the general descriptive name "electron donor–acceptor complexes," used by Briegleb in his well-known book,[7] instead of the name "charge-transfer complexes" which he at first introduced.

Comparison of the Relative Importance of Charge Transfer and Other Forces

Classical electrostatic forces include both Coulomb (*e.g.*, dipole–dipole) and polarization (or "induction," *e.g.*, dipole–induced-dipole) attractive forces. Hanna[2] has recently shown that quadrupole–induced-dipole forces may be comparable in importance to CT forces

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(2) (a) M. W. Hanna, *J. Am. Chem. Soc.*, **90**, 285 (1968); (b) M. W. Hanna and D. E. Williams, *ibid.*, **90**, 5358 (1968); and also see J. L. Lippert, M. W. Hanna, and P. J. Trotter, *ibid.*, in press.

(3) M. J. S. Dewar and C. C. Thompson, Jr., *Tetrahedron Suppl.*, **7**, 97 (1966).

(4) M. Mantione, "Molecular Associations in Biology," B. Pullman, Ed., Academic Press, New York, N. Y., 1948, and references given there.

(5) (a) M. Mantione, *Theoret. Chim. Acta*, **11**, 119 (1968); (b) *Int. J. Quantum Chem.*, in press.

(6) J. P. Malrieu and P. Claverie, *J. Chim. Phys.*, **65**, 735 (1968).

(7) G. Briegleb, "Elektronen-Donator-Acceptor-Komplexe," Springer-Verlag, Göttingen, 1961.

(8) R. S. Mulliken, *J. Chim. Phys.*, **61**, 26 (1964).

in explaining the stability of benzene–I_2 and of similar bπ–aσ[9] complexes. He has also shown that the observed dipole moment of the benzene–I_2 complex must be due, to a nonnegligible extent, to the quadrupole-induced-dipole polarization forces, whereas Mulliken earlier had neglected this possibility and concluded that the observed dipole moment must be due entirely to CT forces. (See also Mantione.[5b])

Besides Hanna, other authors[3–6] have also recently argued the importance, if not preponderance, of Coulomb and polarization forces for the stability of EDA complexes, especially those of the bπ–aπ type (π donor and π acceptor).[2] Mantione[5] has also pointed out that polarization forces can generate dipole moments in such complexes even if neither partner has a dipole moment; in particular, she presents calculations on hydrocarbon–TCNE complexes. For the naphthalene- and pyrene–TCNE complexes, she obtains results in agreement with observed dipole moments. However, this agreement is obtained only by using charges of approximately $+0.4$ e and -0.4 e on the C and N atoms of each CN group in TCNE. On the basis of SCF calculations on related molecules, it seems very improbable that the CN groups contain such large local dipoles. Thus, while polarization must contribute, it seems unlikely that it makes the major contribution in these cases.

Some authors[3,4] have sought to invoke the nonclassical London dispersion forces as making major contributions to the energies of formation of EDA complexes. In the usual case of complexes in *solution*, however, such contributions must ordinarily cancel out to a large extent, since when a complex is formed in solution, the gain in intra-complex dispersion energy is approximately balanced by a loss of solvent–donor and solvent–acceptor dispersion energies.[10] In the vapor state, of course, the dispersion-force contributions must be important.

Some authors[5,6] point out that the wave functions of a complex, including those of its CT states, can be expressed in terms of expansions using only donor and/or acceptor (including *excited state*) wave functions, with no CT terms in the expansion. While this point is valid, it does not contradict the concept of charge transfer, nor is it very helpful in understanding the electronic distribution. It is somewhat analogous to saying that, for example, the electronic wave functions for a molecule can be expressed in terms of excited functions of just one of its atoms instead of by the usual LCAO expressions using AO's of more than one atom. (For example, ψ of HF can be represented using AO's of the F atom only, or ψ of N_2 can be represented using AO's of just one —either one— of the two N atoms.) The reason for using the LCAO procedure for molecules, or for the inclusion of dative (D^+A^-) CT functions in representing the ψ's of EDA complexes, is that such procedures making use of selected members of an overcomplete set of nonorthogonal functions are more economical—more rapidly converging—than the use of a complete orthogonal set of functions. When truncation is necessary, as it is for an approximate description, such a selection procedure represents a sensible and rational mode of description. It is just in this context that one properly speaks of CT forces.

Incidentally, the effect of classical polarization forces on the wave function of a complex can be expressed in terms of an expansion in terms of CT functions, so that classical polarization forces could well be included under the heading of CT forces. For this purpose the no-bond wave function ψ_0 in the usual treatment[10] would be taken as unpolarized. Here, however, we wish to use the term CT forces only for the nonclassical or valence-theoretical CT forces, so that the no-bond wave function ψ_0 is defined to include classical polarization.

Let us now examine some complications bearing on the relative importance of charge transfer and electrostatic forces for some specific types of complexes, particularly the weak bπ–aπ and bπ–aσ complexes,[9] and then conclude with a few comments on the stronger n–aσ complexes (lone-pair donor, σ acceptor).[9]

bπ–aπ Complexes. In the bπ–aπ and bπ–aσ complexes, both donor and acceptor are *sacrificial;* that is, electron transfer involves loss of a bonding electron from the bπ donor and gain of an antibonding electron by the aπ (*e.g.*, TCNE) or aσ (*e.g.*, I_2) acceptor. Hence, CT forces should be especially weak for complexes of these types. In fact most such complexes *are* weak; the values of properties such as the formation constant *K*, the enthalpy of formation $-\Delta H$, and the intensities of CT bands are for the most part relatively small, especially when compared to values for strong n–aσ complexes. In this connection, see Tables I–III, which give representative samples for bπ–aπ and bπ–aσ complexes from Briegleb's extensive tables.[7]

Table I. Some K_x Values[a] (in CCl_4 Solution at 20°)

	Acceptor				
Donor (bπ)	TCNE[b] (aπ)	Chloranil (aπ)	*p*-Benzoquinone (aπ)	TNB[b] (aπ)	I_2 (aσ)
Benzene	10.7	3.4	. . .	24	1.55
Hexamethylbenzene	1530	96	6.0	74	15.7
Phenanthrene	71.5	49	. . .	123	4.5[c]

[a] Values from Briegleb.[7] K_x is the equilibrium constant calculated from equilibrium concentrations expressed in mole fraction units. [b] Abbreviations: TCNE, tetracyanoethylene; TNB, trinitrobenzene. [c] From J. Peters and W. B. Person, *J. Am. Chem. Soc.*, **86**, 10 (1964).

Table II. Some $-\Delta H_x$ Values[a] (kcal) for Complexes in CCl_4 Solution

	TCNE	Chloranil	*p*-Benzoquinone	TNB	I_2
Benzene	3.55	1.65	1.8	1.7	1.3
Hexamethylbenzene	7.75	5.35	(1.8)	4.7	3.73
Phenanthrene	4.30	3.65	1.8	4.3	1.6

[a] Values from Briegleb,[7] except for phenanthrene–I_2 (see footnote *c* of Table I).

As discussed above, the stability of these weak complexes must be attributed in appreciable part to

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(9) Many authors used Dewar's term "π complexes" for complexes with π donors (or acceptors). However, a more precise terminology[10] (see also ref 8) which specifically indicates both the donor type and the acceptor type seems preferable.

(10) R. S. Mulliken and W. B. Person, "Molecular Complexes, A Lecture and Reprint Volume," John Wiley and Sons, Inc., New York, N. Y., 1969.

Table III. Some Absorption Intensity[a] Values for the CT Band (in CCl_4 Solution[b])

	TCNE[b]	Chloranil	p-Benzoquinone	TNB	I_2
Benzene	3570	2350		5855	15,000
Hexamethylbenzene	4390	2650	2016	2150	6,700
	(6230)	(3950)	(2960)	(3000)	(8,430)
Phenanthrene	. . .	887		1375	7,100[c]

[a] Values given are ϵ_{max}, from ref 7, corrected to be proportional to D in the case of those in parentheses by multiplication by the ratio of ν_{max} in benzene to ν_{max} in hexamethylbenzene. [b] TCNE in CH_2Cl_2 solution. [c] From reference given in footnote *c* of Table I.

the action of classical Coulomb and/or polarization forces. On the other hand, the same considerations or causes which require CT forces to be predominantly responsible for the stability of strong n–v and n–σ complexes must still be at work in weaker complexes: hence CT forces must make at least *some* contribution to the stability of weak EDA complexes. Some of these considerations are now summarized.

The fact that all properties which are related to the strengths of bπ–aπ complexes are usually fairly well correlated[7] with familiar measures of electron donor and acceptor tendencies (especially with the magnitudes of ionization potential of donor and electron affinity of acceptor) seems to be a major argument in favor of the importance of CT forces for the strengths of the stronger of these complexes. In particular, the values of these properties increase in a fairly regular way through a series of complexes involving different donors with a common acceptor as the ionization potential of the donor decreases. Such trends, which explain changes in strength between molecular pairs for which there is no obvious reason to suppose much change in the electrostatic interaction, support the existence of nonnegligible CT forces in such complexes.

Consistent with this view is the usual absence of evidence of complex formation between like or nearly like molecules—even those which might be expected to exhibit some electrostatic forces of attraction, as, for example, between two molecules of trinitrobenzene or of benzene—or between benzene and the very weak acceptor nitrobenzene (in contrast to the definite formation of a benzene complex with the stronger acceptor trinitrobenzene). The fact that complete electron transfer occurs (usually with some assistance, for example, in polar solvents or in crystal formation) in bπ–aπ inner complexes built from especially strong donors and acceptors forms a natural climax to the enhanced importance of CT forces in the corresponding outer complexes. (On this point, see the further discussion near the end of this section.)

Some comments on Tables I–III are now in order. More complete tables would show a fairly steady progression in K and $-\Delta H$ (and usually in CT band intensity) in each series of complexes between a given acceptor and a series of donors beginning with benzene and substituting methyl groups to end with hexamethylbenzene. As we expect if CT forces are important, increasing stability accompanies increasing donor ability as measured by decreasing donor ionization potential I_D (which drops from 9.24 eV in benzene to 7.85 eV in hexamethylbenzene). However, it can also be argued that the increases in $-\Delta H$ and K are due in considerable part to increasing electrostatic effects caused as the methyl groups are substituted in the benzene ring. For example, the relatively large K and $-\Delta H$ for the hexamethylbenzene–TCNE complex might perhaps be so explained.

More direct measures of the extent of CT should perhaps be the CT band intensities. According to CT theory, dipole strengths D of the CT bands should increase with increasing extent of CT in the ground state of the complex. The oscillator strength f of a band is proportional to $\int\epsilon_\nu d\nu$, taken over the band, and this in turn, for bands of equal half-width, is proportional to the peak absorptivity ϵ_{max} in the band. On the other hand, f is proportional to $\nu_{max}D$; thus D is approximately proportional to ϵ_{max}/ν. Thus to compare D values for benzene and hexamethylbenzene complexes, one may compare ϵ_{max}/ν values; in Table III values of ϵ_{max} corrected by the ratio of ν_{max} values for benzene and hexamethylbenzene are therefore given (in parentheses) for hexamethylbenzene. It is seen that these values show for hexamethylbenzene a moderate increase in dipole strength for the CT band over that for benzene in the case of the TCNE and chloranil complexes, indicating a moderate increase in extent of CT.[11] Comparison of the data for the hexamethylbenzene complexes of chloranil with the benzene complexes shows much greater differences in K and $-\Delta H$ than occur for ϵ_{max} values, suggesting perhaps that the stabilities of chloranil complexes are being influenced by electrostatic forces.

The fact that stabilities (K, $-\Delta H$) for complexes of a given acceptor with phenanthrene (I_D = 8.1 eV) sometimes increase and sometimes decrease from those for hexamethylbenzene (I_D = 7.85 eV) suggests that other than CT effects are also important. However, the variability in these results is not obviously accounted for by electrostatic forces. The intensities for the phenanthrene and hexamethylbenzene complexes with I_2 are approximately equal, as expected, but the intensity results from the other complexes are variable, again suggesting that an explanation involving both CT and electrostatic forces is needed.

In connection with the present discussion, the following point deserves mention. Clearly it would be preferable to compare the predictions of theory with vapor phase data on complexes rather than with the solution data of Tables I–III. However, such comparisons with the limited vapor data now available are not very enlightening. Kroll[12] in his vapor-phase study of complexes of TCNE with methylated benzene donors finds very little change in the intensity of the CT band (if anything, there is some decrease in intensity) as the number of methyls increases, suggesting little change in CT through that series. Although these data contradict the conclusion reached from the variation in solution intensities of bπ–TCNE complexes, it is not clear that the vapor-based conclusion is to be preferred.

(11) However, the TNB complexes fail to fit into the picture, indicating that the theoretical explanation must be more complex. Actually, the CT intensity expression *is* more complex,[10] but not in such a way as to offer a ready explanation. In the case of the I_2 complexes of the methylated benzenes, if the "axial model" is correct (see next section), the usual theory is inapplicable,[10] so that the observed decrease in intensity with methylation is not relevant evidence on the extent of CT. In general, contributions to the intensity from admixture of the CT state with locally excited states must be considered.

(12) M. Kroll, *J. Am. Chem. Soc.*, **90**, 1097 (1968).

The intensities of the CT band as obtained in the vapor phase are considerably lower than in solution. The reason for this phenomenon is not clear. One suggestion is that the solvent cage around the complex in solution confines it so that it is under some pressure with resulting higher overlap and increased CT.[13]

The experimental observation that the intensities of the CT bands of typical bπ–aπ complexes increase greatly with increasing external pressure[14] is exactly what is predicted from a theory in which CT forces play a *small* but *not negligible* part in accounting for the stabilities of complexes. Namely, let the wave function of the complex be written in the form

$$\Psi(\mathrm{D{-}A}) = a\Psi_0(\mathrm{D,A}) + b\Psi_1(\mathrm{D^+{-}A^-}) + \dots \qquad (1a)$$

or more generally

$$\Psi(\mathrm{D{-}A}) = a\Psi_0(\mathrm{D,A}) + \sum_i b_i\Psi_i(\mathrm{D^+{-}A^-}) + \dots \qquad (1b)$$

with b^2/a^2 (or $\Sigma b_i^2/a^2$) $\ll 1$ for a weak complex. The extent of CT action is measured for a normalized function (eq 1a) by $F_{1\mathrm{N}} = b^2 + abS_{01}$, the fraction of charge transferred from donor to acceptor in the complex; S_{01} is the overlap of Ψ_1 with Ψ_0. The magnitude of CT, and with it the intensity of CT bands, is expected to depend on the extent to which donor and acceptor overlap. If the overlap is small in the absence of external pressure, as is expected for very weak complexes, it should be especially sensitive to external pressure, since for small enough initial overlap of two molecules, the overlap must increase exponentially as they are squeezed together.[15]

The relation observed, for a series of complexes formed from a series of donors and any one acceptor, between the energy change $h\nu_{\mathrm{CT}}$ corresponding to the CT band (in particular, the *first* CT band) of one of the complexes and the minimum ionization potential I_{D} of the donor, is another possible source of information concerning the amount of charge transfer. For weak complexes, to the extent that eq 1a is accurate, this relation is expected to be of the form

$$h\nu_{\mathrm{CT}} = I_{\mathrm{D}} - C_1 + C_2/(I_{\mathrm{D}} - C_1) \qquad (2)$$

with C_1 and C_2 perhaps substantially constant for the given series of complexes.[16] Here C_1 is determined predominantly, for weak complexes, by the classical Coulomb energy of attraction, $-C$, between $\mathrm{D^+}$ and $\mathrm{A^-}$. The second term $C_2/(I_{\mathrm{D}} - C_1)$ is the CT resonance energy term and is related to b/a of eq 1; in the absence of charge transfer, both C_2 and b would be zero. A detailed discussion of the application of eq 2 to an evaluation of the extent of CT in bπ–aπ and bπ–aσ complexes is given in ref 10. On the whole, no very certain conclusions are reached in this way.

For most of the known bπ–aπ complexes, $h\nu_{\mathrm{CT}}$ is in the visible. From the theory[10] one sees that when $I_{\mathrm{D}} - C_1$ of eq 2, hence ν_{CT}, is especially small, the amount of CT must increase, roughly as $(\nu_{\mathrm{CT}})^{-2}$. Thus for the TMPPD (tetramethyl-*p*-phenylenediamine) complex with CHl (chloranil), with ν_{CT} in the infrared[17] near 11,500 cm^{-1}, the amount of CT should be roughly five times as large as for benzene–TCNE (which[18] has ν_{CT} about 26,000 cm^{-1}), or about 15% CT if there is 3% for benzene–TCNE. That this estimate is if anything an underestimate is indicated by the ease of formation of the ions TMPPD$^+$ and CHl$^-$ in even moderately polar solvents. Taking this reasoning into account, it seems to be established that while the amount of CT is small, or even very small, for the weaker bπ–aπ complexes it becomes large in those where I_{D} is sufficiently small.

bπ–Halogen Complexes. In the 1:1 complexes of iodine or of other halogens (ICl, $\mathrm{Br_2}$, $\mathrm{Cl_2}$) acting as aσ acceptors with bπ donors, CT action in both donor and acceptor is again sacrificial, and one expects weak complexes. In fact (see Tables I–III), K and $-\Delta H$ are again observed to be relatively small for these complexes. However, the CT bands are surprisingly strong, suggesting the existence of rather large charge transfer. Other measures of the fraction of charge transferred ($F_{1\mathrm{N}}$) suggest that the extent of CT is not very large. For example, the shift of the halogen-halogen stretching frequency suggests $F_{1\mathrm{N}} \approx 0.03$ for benzene-$\mathrm{I_2}$, while the dipole moment for the complex, ignoring any quadrupole-induced dipole,[2a] suggests $F_{1\mathrm{N}} \approx 0.07$ to 0.11, depending upon the assumptions made for the geometry of the complex.[10] Such estimates for $F_{1\mathrm{N}}$ are consistent with a CT resonance energy of from 0.7 to 2.5 kcal/mole,[10] which is comparable to the observed $-\Delta H_{\mathrm{f}}$ of about 1.5 kcal/mole.[7] Hence we may conclude that the extent of CT is probably rather small, but that it may still contribute appreciably to the stability of the complex in this case.

On the other hand, pure quadrupole spectroscopy data,[19] likewise data on Br–Br interatomic distance,[20] for the benzene–$\mathrm{Br_2}$ complex in the solid state, indicate that the amount of charge transfer to the $\mathrm{Br_2}$ here is very small. To be sure, the solid complex is not the 1:1 complex which we have been discussing but is built of alternating chains of benzene–bromine–benzene... molecules, with an axial orientation of each $\mathrm{Br_2}$ along the sixfold axes of the two benzene molecules between which it lies.[20] Still, it seems likely that if there is very little charge transfer in the solid complex, the same is true in the 1:1 complex.[21]

However, it is not clear just how much increase in the length of the Br–Br bond (or change in the

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(13) J. Prochorow and A. Tramer, *J. Chem. Phys.*, **44**, 4545 (1966).

(14) (a) J. R. Gott and W. G. Maisch, *ibid.*, **39**, 2229 (1963); (b) H. W. Offen and collaborators, *ibid.*, **42**, 430 (1965); **45**, 269 (1966); **47**, 253, 4446 (1967), and later papers.

(15) The argument given here is probably conclusive, but *possibly* not, since b^2/a^2 depends on the overlap integral for a bonding donor MO ϕ_{D} not with an occupied acceptor MO, but with a normally unoccupied $\mathrm{A^-}$ acceptor MO $\phi_{\mathrm{a^-}}$ (see ref 10, sections 3-4 and 3-5). If the overlap of ϕ_{d} with the relatively larger orbital $\phi_{\mathrm{a^-}}$ were appreciable when neutral A (with its smaller orbital, ϕ_{a}) is not yet overlapping neutral D, the argument would fail. This situation seems improbable for bπ–aπ complexes, where most likely $\phi_{\mathrm{a^-}}$ is in fact scarcely bigger than the size of the acceptor. (The *size* of the acceptor is all that is relevant here; it is not necessary that any particular overlap *integral* of D and A MO's be nonzero.)

(16) See ref 10, eq 9-7 and 9-4, or see R. S. Mulliken and W. B. Person, *Ann. Rev. Phys. Chem.*, **13**, 107 (1962).

(17) R. Foster and T. J. Thomson, *Trans. Faraday Soc.*, **58**, 860 (1962).

(18) R. E. Merrifield and W. D. Phillips, *J. Am. Chem. Soc.*, **80**, 2778 (1958).

(19) (a) H. O. Hooper, *J. Chem. Phys.*, **41**, 599 (1964). This paper also finds evidence of very little charge transfer in the complexes of *p*-xylene with $\mathrm{CBr_4}$ and $\mathrm{CCl_4}$, but these bπ–aσ complexes are of an extremely weak type so that very little charge transfer would be expected. (b) D. F. R. Gilson and C. T. O'Konski, *ibid.*, **48**, 2767 (1968).

(20) O. Hassel, *Mol. Phys.*, **1**, 241 (1958).

(21) The fact that the $\mathrm{Br_2}$ is symmetrically located in the solid complex, so that, unlike the case of the 1:1 complex with its unsymmetrical location of the $\mathrm{Br_2}$, no dipole moment can be created, should not inhibit (though perhaps it could modify) the occurrence of charge transfer.

quadrupole resonance frequency) should be expected for a nonnegligible amount of charge transfer. It seems reasonable to expect that the increase in Br–Br distance might be approximately linear with F_{1N}. For the strong aliphatic amine–X_2 complexes ($F_{1N} \approx 0.4$) the increase in the X–X bond length from that in the free halogen is about 0.25 Å. Hence, we might expect an increase in Br–Br length for benzene–Br_2 of about one-eight to one-fourth of that value or from 0.03 to 0.06 Å (F_{1N} from 0.05 to 0.10). This increase is only slightly greater than the experimental uncertainty in the X-ray work, and we suspect that this argument can be made conclusive only if a very careful X-ray study is made. If there is nonnegligible CT in the benzene–Br_2 crystal, we also expect the benzene–Br distance to be less than the van der Waals distance. Experimentally, this distance is found to be 3.36 Å compared to 3.65 Å expected for the sum of van der Waals radii. Hence we believe the X-ray results are ambiguous but are also consistent with small but nonnegligible CT. A similar statement applies[19b] to the quadrupole resonance results.

Complexes of n–aσ Type. There is no question that classical Coulomb and polarization forces can play only a minor part as compared with CT forces in accounting for the large observed $-\Delta H$ and K values and dipole moments[10] of the strong n–aσ complexes of iodine with the aliphatic amines. As a check on this conclusion, Dr. M. Itoh has very kindly computed the classical dipole-induced–dipole contributions to the stabilization energies and the dipole moments of NH_3–I_2 and of $(CH_3)_3N$–I_2, following the procedure used by Hanna,[2a] and has obtained the results given in Table IV. Hence, there must indeed be considerable charge transfer in these stronger complexes; judging from the dipole moments, $F_{1N} \approx 0.4$. Moreover, K_x, $-\Delta H$, and CT band intensity all increase together in these complexes with increasing donor strength, in agreement with the CT theory.

Table IV. Polarization Contributions to Stability and Dipole Moments of Amine–Iodine Complexes[a]

	Major computed polarization contributions					
	Approx 1		Approx 2		Observed	
Complex	μ, D	W, kcal	μ, D	W, kcal	μ, D	$-\Delta H$, kcal
H_3N–I_2	0.91	0.34	1.96	1.58	~6.4	4.8
$(H_3C)_3N$–I_2	0.30	0.04	0.57	0.13	~6.0	10.2

[a] The approximations 1 and 2 are those of Hanna.[2a] The data used are: μ of NH_3, 1.5 D, μ of $(CH_3)_3N$, 0.63 D; dimensions of $(CH_3)_3N$–I_2, ref 20: I_2 polarizability, ref 2a; observed μ, see ref 10, Table 6-2. W = energy. In the computations, a point dipole located at the midpoint of the NH or CN bond was assumed.

Because so many of the properties of the n–aσ complexes appear to be correlated as logical extensions of the CT theory of weak complexes, it is clear that some CT also occurs in the weaker complexes. We concur with the conclusions of Hanna[2a] that the extent of CT action may have been overestimated for weak complexes in the past, but that it still involves forces whose magnitude is at least comparable to the electrostatic forces for most weak complexes. The predominance of CT forces in the n–aσ iodine complexes make them a useful limiting test case. The rather smooth variation of CT-dependent properties of the complexes from the weak bπ–aπ or bπ–aσ complexes to the strong n–aσ complexes indicates that the extent of CT varies from very little ($F_{1N} \approx 0.01$) to large ($F_{1N} \approx 0.4$) in a similar way.

Reactions of Gaseous Ions. XVII. Methane + Unsaturated Hydrocarbons

M. S. B. Munson[1a] and F. H. Field[1b]

Contribution from Baytown Research and Development Division, Esso Research and Engineering Company, Baytown, Texas, and Corporate Research Laboratories, Esso Research and Engineering Company, Linden, New Jersey. *Received December 23, 1968*

Abstract: Rapid proton transfer reactions are observed between CH_5^+ and ethylene, propylene, and isobutylene. However, CH_5^+ adds to acetylene to give mostly $C_3H_5^+$ by a second-order process and $C_3H_7^+$ by a collision-stabilized addition reaction. $C_2H_5^+$ also reacts predominantly by proton transfer with propylene and isobutylene, but adds to ethylene and acetylene in collision-stabilized processes. Three-body alkylation reactions were observed for $C_2H_5^+$ and C_2H_4 and $C_3H_7^+$ and C_3H_6 to a much greater extent than for $C_4H_9^+ + i$-C_4H_8. Estimates are made for lifetimes of collision complexes for several reactions.

In previous publications,[2] we studied the ionic reactions in methane at pressures as high as 2 Torr and the effects of several additives on the ionic distributions. The present paper reports the ionic reactions in mixtures of methane with approximately 1% of a few unsaturated hydrocarbons. Since unsaturated hydrocarbons are produced in the irradiation of methane, we feel that these results will be pertinent to radiation chemistry. In addition, these experiments are part of a systematic study of the reactions of CH_5^+, and we had expectations

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[1] (a) Baytown Research and Development Division; present address: Department of Chemistry, University of Delaware, Newark, Del. 19711. (b) Corporate Research Laboratories.

[2] (a) F. H. Field and M. S. B. Munson, *J. Am. Chem. Soc.*, 87, 3289 (1965); (b) M. S. B. Munson and F. H. Field, *ibid.*, 87, 3294 (1965); (c) *ibid.*, 87, 4242 (1965).