Table V. Theromdynamic Data[a]

Species	ΔH_f	Ref	Species	ΔH_f	Ref
$(CH_3CN)_2H^+$	$\leqslant 221$	*b*	$N_2\cdot^+$	359	*e*
$C_3H_4N^+$	$\leqslant 271$	6	H_2CN^+	224	4
CH_3CNH^+	200	4	$HCN\cdot^+$	351	*e*
$CH_3CN\cdot^+$	303	6	HCN	31.2	*h*
CH_3CN	21.0	*c*	$C_2H_2\cdot^+$	317.1	*i*
CH_2CN^+	281	6	C_2H_2	54.2	*i*
$CH_2CN\cdot$	55	*d*	$C_2H\cdot$	115	*i*
$CHCN\cdot^+$	~ 369	*e*	CH_3^+	261	*e*
CHCN	107	*f*	$CH_2\cdot^+$	332	*i*
$CCN\cdot$	123	*g*	CH_2	91.9	21
$CN\cdot$	109	*d*	$CH\cdot$	142	*d*
N_2H^+	253	5			

[a] Heats of formation (kilocalories per mole) are for the gas phase at 298°K. [b] Based on observation of proton-bound dimer. [c] J. S. Roberts and H. A. Skinner, *Trans. Faraday Soc.*, **45**, 339 (1949). [d] J. A. Kerr, *Chem. Rev.*, **66**, 465 (1966). [e] F. H. Field and J. L. Franklin, *Pure Appl. Phys.*, **1**, 249 (1957). [f] Assuming D(C–H) = 104 kcal/mol, ΔH_f(CHCN) = ΔH_f(CH$_2$CN) − ΔH_f(H·) + D(C–H). [g] V. H. Diebler, R. M. Reese, and J. L. Franklin, *J. Amer. Chem. Soc.*, **83**, 1813 (1961). [h] S. W. Benson, *J. Chem. Educ.*, **42**, 502 (1965). R. R. Bernecker and F. A. Long, *J. Phys. Chem.*, **65**, 1565 (1961).

Table VI. Proton Affinities and Heats of Formation[a]

Species (M)	ΔH_f (M)[b]	ΔH_f (M$^+$)	ΔH_f (MH$^+$)	PA (M)
$(C_2H_5)_2O$	−60.3	159	106	199
$(CH_3)_2CO$	−51.8	171	125[c]	188[c]
CH_3CN	+21.0[d]	303[e]	200[f]	186[f]
CH_3CHO	−39.7	195	143	184[c]
CH_3OH	−48.1	202	142	175

[a] All thermodynamic quantities are given in kilocalories per mole. Unless otherwise noted, data are from ref 18. [b] J. H. S. Green, *Quart. Rev.* (London), **15**, 125 (1961). [c] A. G. Harrison, A. Ivko, and D. Van Raalte, *Can. J. Chem.*, **44**, 1625 (1966). [d] J. S. Roberts and H. A. Skinner, *Trans. Faraday Soc.*, **45**, 339 (1949). [e] Reference 6. [f] Reference 4.

formation of CH_2. A large number of other ion–molecule reactions were observed in the above mixtures but will not be discussed here.

Summary

The ion–molecule chemistry of acetonitrile is indeed complex and interesting from many points of view. Icr is clearly of great utility in establishing the detailed ion–molecule chemistry. The techniques of isotopic labeling are valuable in unraveling overlapping reaction pathways and describing some of the important aspects of specific reaction mechanisms. The observation of higher mass ions serves to substantiate the importance of considering ion–molecule reactions as a means of obtaining complex molecules and should lead to further emphasis in the study of discharges as potential synthetic techniques.

These experiments demonstrate the power of icr in the analysis of complex gas phase chemistry. The finding of selective mechanisms in several reactions should lead to further emphasis in the search for and interpretation of parallels in solution chemistry where selective reactions are routine, and should encourage further study of reaction mechanisms in solvent-free systems, not only to study the reactions themselves, but also to gain a better feeling for the importance of solvent effects.

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Dipole Moments and Charge-Transfer Parameters of the Iodine Complexes of Some Oxygen and Sulfur Donors[1]

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Contribution from the Department of Chemistry, Indian Institute of Technology, Kanpur, India. *Received May 18, 1968*

Abstract: Dipole moments of the charge-transfer complexes of some sulfur (sulfide and thiocarbonyl) and oxygen (ether and carbonyl) donors with iodine have been determined and the various charge-transfer parameters have been calculated by making use of the charge-transfer transition energies and heats of formation of the complexes. The contribution of the charge-transfer structure in the ground state appears to be greater in the complexes of sulfur donors than in the complexes of oxygen donors.

Dipole moments of charge-transfer complexes provide valuable information on the nature of binding in the ground states of the complexes. In the literature, the dipole moments of the halogen complexes of aromatic hydrocarbons[3] and amines[4] have been reported. Recent studies on the spectroscopy and thermodynamics of the charge-transfer complexes of iodine with carbonyl and thiocarbonyl compounds have shown

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(1) Taken in part from the Ph.D. thesis (1968) of S. N. B., Indian Institute of Technology, Kanpur, India.

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(3) S. P. McGlynn, *Chem. Rev.*, **58**, 1113 (1958).

(4) S. Kobinata and S. Nagakura, *J. Amer. Chem. Soc.*, **88**, 3905 (1966).

that the adducts with thiocarbonyl compounds are associated with higher equilibrium constants and enthalpies of formation.[5-8] The results seemed to indicate a greater contribution of the CT structures in the complexes of thiocarbonyl donors. We have presently investigated the dipole moments of the iodine complexes of a few sulfur (sulfide and thiocarbonyl) donors and oxygen (ether and carbonyl) donors and have evaluated the various charge-transfer parameters with the aid of Mulliken's theory.[9-11]

Results and Discussion

It was first ascertained that under the conditions of the experiments, all the iodine molecules in solution had indeed formed 1:1 complexes with the donors. Thus the measured dielectric constants (as well as the densities) of the solutions showed linear relations with the weight fractions of the complexes indicating that there was little or no dipole–dipole interaction between the complexes. Similarly, it was found that there was no ion-pair formation sufficient to affect the measurements.

According to the charge-transfer theory of Mulliken,[9-11] the ground- (ψ_G) and excited- (ψ_E) state wave functions of a charge-transfer complex may be written as

$$\psi_G = a\psi_0 + b\psi_1 \tag{1}$$

$$\psi_E = a^*\psi_1 - b^*\psi_0 \tag{2}$$

where ψ_0 and ψ_1 represent the wave functions for the no-bond and CT structures, respectively. The dipole moment of the ground state, μ_G, which is experimentally determined, is given by

$$\mu_G \approx a^2\mu_0 + b^2\mu_1 + abS\mu_0 + abS\mu_1 \tag{3}$$

where S is the overlap integral between ψ_0 and ψ_1 and μ_0 and μ_1 are the dipole moments of the no-bond and CT structures, respectively. If $\mu_0 \approx 0$, eq 3 simplifies to

$$\mu_G \approx b^2\mu_1 + abS\mu_1 \tag{4}$$

With the aid of eq 3 or 4 one can evaluate a and b making use of the normalization condition, $a^2 + b^2 + 2abS = 1$. On the basis of the various relations[10,11] among the ground-state (W_B) and excited-state (W_E) energies, the heat of formation (ΔH°), and the charge-transfer transition energy ($h\nu_{CT}$), it can be shown that[12]

$$h\nu_{CT} = W_E - W_G = (W_1 - W_0) + (X_1 - X_0) = \beta_0\{[(k - k^*)/kS] - [(k + S)^2 + k^2(1 - S^2)]/[k(1 + kS)(1 - S^2)]\} \tag{5}$$

where W_0 and W_1 are the energies of the no-bond and CT structures, respectively, X_0 and X_1 are the resonance energies in the ground and excited states, respectively, and β_0 and β_1 are the resonance integrals. Further, we have the relations

$$k = b/a;\ k^* = b^*/a^* = (k + S)/(1 + kS) \tag{6}$$

$$X_0 = k\beta_0/(1 + kS);\ -X_1 = k^*\beta_1/(1 - k^*S) \tag{7}$$

$$\beta_1 = k^*\beta_0/k;\ (W_1 - W_0) \approx (\beta_0 - \beta_1)/S \tag{8}$$

and

$$W_G = -\Delta H^\circ \tag{9}$$

It must be noted that we have assumed in these calculations that the dipole moment of the complex is entirely due to the charge transfer in the ground electronic state of the complex. We have ignored any possible contribution from quadrupole–dipole interactions to the ground-state properties of the complexes.[13]

In order to estimate S and μ_1, we need to know the geometrical configurations of the complexes. It was assumed that the iodine molecule (I–I = 2.84 Å) is collinear with the oxygen (or the sulfur) atom of the donor and that the negative and positive charges in the CT structure are at the center of the iodine molecule and the oxygen (or the sulfur) atom, respectively.[4,9] The O–I and S–I distances were taken to be 2.75 and 2.80 Å, respectively.[14,15] The values of μ_1 thus calculated for the iodine complexes of oxygen and sulfur donors were 19.93 and 20.35 D, respectively. The coefficients a and b and other charge-transfer parameters were calculated by assuming $S = 0.1$ and 0.3, since the systems studied presently seem to vary between relatively weak to strong CT complexes.[10,11,16] Among the donors studied, $\mu_0 = 0$ only in the cases of dithiane and dioxane and eq 4 could be used for the evaluation of a and b in these two cases.

The results of the calculations with $S = 0.1$ and $S = 0.3$ are summarized in Table I. The contributions of the CT structures in the ground state (per cent CT) of the complexes have been calculated as $100(b^2 + abS)$. The % CT varies from ~9 to ~23% in the complexes of sulfur donors and from ~6 to ~11% in the complexes of oxygen donors. The values of % CT are only slightly different when $S = 0.3$ compared to when $S = 0.1$, but % CT is always greater with the sulfur donors compared to the oxygen donors. On the basis of these results we may conclude that the sulfur donors are better bases than the corresponding oxygen donors; both the sulfur and oxygen donors are, however, much weaker bases than amines.[4] The energies of the no-bond structures (W_0) are always positive when $S = 0.1$, indicating that the structures are repulsive. The W_0 values become slightly negative when $S = 0.3$ in most cases except for the complexes of ethyl thiocarbamate and dimethylformamide, where the % CT values are also highest. When W_0 is positive, the resonance stabilization energy (X_0) is larger than the heat of formation (ΔH°) of the complex; when $S = 0.3$ and W_0 is negative, X_0 is less than ΔH°. Since the O–I (or the S–I) distance is considerably shorter than the van der Waals distance between O and I (or S and I) the no-bond structures would be expected to be repulsive. It therefore appears reasonable to employ $S = 0.1$ in all the systems studied presently.

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Table I. Dipole Moments and Charge-Transfer Parameters

Donor	μ_0[a]	μ_G[a]	S	a	b	CT, %[b]	$-\beta_0$	$-\beta_1$	$-X_0$	X_1	W_0	W_1	$h\nu$, ct[c]	$-\Delta H°$[c]
1,4-Dithiane	0.0	2.15	0.1	0.93	0.28	10.6	1.08	1.40	0.32	0.57	0.05	3.21	4.05	0.27
			0.3	0.91	0.22	10.6	0.78	1.65	0.17	0.97	−0.10	2.81		
Dimethyl sulfide	1.40	3.62	0.1	0.92	0.30	11.7	1.16	1.47	0.36	0.63	0.03	3.14	4.11	0.34
			0.3	0.91	0.23	11.7	0.85	1.71	0.20	1.04	−0.14	2.73		
Ethyl isothiocyanate	3.67	5.09	0.1	0.94	0.25	8.4	1.02	1.38	0.26	0.50	0.11	3.64	4.30	0.15
			0.3	0.93	0.18	8.5	0.71	1.68	0.13	0.92	−0.02	3.22		
Ethylene trithiocarbonate	4.47	5.86	0.1	0.94	0.25	8.6								0.36
			0.3	0.93	0.19	8.9								
Tetramethylthiourea	4.70	7.52	0.1	0.89	0.38	18.0	1.30	1.53	0.54	0.82	0.12	2.47	3.71	0.41
			0.3	0.86	0.31	18.0	1.01	1.66	0.33	1.21	−0.08	2.08		
Ethyl thiocarbamate	3.24	7.12	0.1	0.86	0.44	22.7	1.58	1.81	0.76	1.11	0.44	2.65	4.08	0.32
			0.3	0.83	0.37	22.7	1.28	1.89	0.50	1.55	0.18	2.21		
1,4-Dioxane	0.0	1.30	0.1	0.96	0.21	6.5	0.96	1.37	0.21	0.44	0.06	4.10	4.69	0.15
			0.3	0.94	0.15	5.6	0.63	1.75	0.10	0.88	−0.06	3.66		
Tetramethylurea	3.66	5.20	0.1	0.94	0.26	9.4	1.16	1.53	0.32	0.59	0.13	3.82	4.59	0.19
			0.3	0.92	0.20	9.5	0.82	1.83	0.17	1.04	−0.02	3.37		
Dimethylformamide	3.84	5.56	0.1	0.93	0.28	10.7	1.31	1.69	0.39	0.69	0.22	4.00	4.86	0.17
			0.3	0.91	0.22	10.7	0.94	1.98	0.21	1.17	0.04	3.52		

[a] The dipole moments are in Debyes (solvent, CCl_4; temperature, 30°). The μ_0 values of ethylene trithiocarbonate and ethyl thiocarbamate are from the present study; the other μ_0 values are from A. L. McClellan, "Tables of Experimental Dipole Moments," W. H. Freeman and Co., San Francisco, Calif., 1963. [b] $\%\ \mathrm{CT} = 100(b^2 + abS)$. [c] In electron volts; from ref 5–8.

Experimental Section

All the compounds used in the study except ethyl thiocarbamate were available commercially; they were purified by fractionation. Ethyl thiocarbamate was prepared by the reaction of ethyl isothiocyanate with methanol. Dry Analar CCl_4 was employed as the solvent for all the measurements.

The dielectric constants of solutions were measured employing a dipole meter (WTW GmbH, Germany, Model DM01) fitted with a cylindrical gold-plated condenser cell (Type DFL2). The instrument operated on the superposition (beat) method. The temperature of measurement was 30 ± 0.2°. Densities of solutions were measured with an Ostwald–Sprengel pycnometer. The dipole moments of all the donors except ethyl thiocarbamate and ethylene trithiocarbonate were available in the literature.[17]

In the dielectric measurements of the complexes, the concentration of iodine ranged from 0.003 to 0.07 *M* and did not exceed one-tenth of the donor concentration. It was ascertained by parallel measurements of the electronic absorption spectra that all the iodine molecules in solution had complexed with the donor molecules. There was no evidence of triiodide ions in solutions as shown by measurements of the absorption spectra in the regions of 297 and 363 mμ where the triiodide ion has intense absorption bands. Measurements of both the absorption spectra and dielectric constants as functions of time showed that there were no time-dependent processes leading to ion pair formation.[18] In practice, the iodine solution maintained at 30° was added to the solution of the donor at 30° just prior to the measurements.

The dielectric constants (as well as the densities of solutions) when plotted against the weight fraction of the complexes showed excellent linearity. The details of the method employed for the calculation of the dipole moments of the complexes are similar to those described by Kobinata and Nagakura.[4]

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(17) See McClellan, Table I, footnote *a*.

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