k_2 an estimate of k_i was made by comparison with k_i values in the other compounds. The force constants in Table III for this compound are therefore put in parentheses.

Summary.—The results in Table III clearly show that the five rules proposed are entirely consistent with all the experimental data. Using rules 1 and 2 the force constants in Table III were obtained and they in turn are in complete accord with the expectations from rules 3–5. Thus there are steady decreases in k_1 and k_2 as the number of substituents increases (rule 3); CO's *cis* to substituents have higher k's than those *trans* (rule 4); and there is an upward trend in the k_i's with increasing substitution (rule 5).

It is also interesting to note that the compounds of the same type with Cr, Mo and W as the metal atom have force constants which do not differ significantly. This implies that the extent of pi bonding does not vary much with atomic number for metal atoms in the same group in analogous compounds.

[CONTRIBUTION FROM THE LABORATORY OF MOLECULAR STRUCTURE AND SPECTRA, DEPARTMENT OF PHYSICS AND DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CHICAGO, CHICAGO 37, ILL.]

Molecular Complexes and their Spectra. XV. Iodine Complexes with Thiophene, 2-Methylfuran and N-Methylpyrrole

BY ROBERT P. LANG

RECEIVED APRIL 30, 1962

The thermodynamic and electronic spectral characteristics of the 1:1 molecular complexes of iodine with thiophene, 2-methylfuran and N-methylpyrrole have been determined from absorption spectrophotometric studies of *n*-heptane solutions. Partial studies were made with furan and pyrrole. In the case of pyrrole a reaction with iodine, producing a precipitate, was found to take place. For the furans and the pyrroles two distinct charge transfer bands were detected. These results show a considerable reduction in electron donor strength for these donors compared to the corresponding sulfides, ethers and amines and are in agreement with the well-known aromatic character of these compounds.

Introduction

Both the chemistry and the physical properties of thiophenes, furans and pyrroles indicate that these compounds have considerable aromatic character; in addition, quantum mechanical calculations support this view.[1] In fact, these compounds behave more like aromatic hydrocarbons than like unsaturated sulfides, ethers and amines.

The thermodynamic and electronic spectral characteristics of iodine complexes with a variety of both n-donors[2] and π-donors[3] have been studied. In general, the K, ΔH° and the "blue shift" of the visible iodine band for the 1:1 iodine complexes are substantially larger for n-donors compared to aromatic π-donors like benzene. Consequently, it should be of considerable interest to compare these characteristics for the iodine complexes of thiophenes, furans and pyrroles with those of the corresponding sulfides, ethers and amines, all n-donors.

Experimental

Materials.—Fisher Certified iodine was resublimed under reduced pressure. Phillips 66 "pure" grade *n*-heptane was washed twice with concentrated sulfuric acid, then three times with water, dried with Drierite and distilled with a Podbielniak column. Matheson Coleman and Bell thiophene was treated with activated silica gel, alumina, Drierite and finally distilled with a Podbielniak column. The distillate was stored over alumina for several days with occasional shaking. Gas chromatography showed no detectable impurities. The final purified thiophene had an odor similar to that of benzene; and *n*-heptane solutions of thiophene, with constant initial iodine concentration, showed an isosbestic point at about 525 mμ for the free and shifted visible iodine bands, indicating that the iodine was not reacting with thiophene or with any impurities in the solutions. (Impure thiophene gave spectra that came below the isosbestic point by 10–20% of the absorbance of the visible iodine band indicating that some reaction was taking place between iodine and an impurity.)

Eastman Kodak Co. practical grade 2-methylfuran and furan were dried over Drierite and then purified by fractional distillation from potassium hydroxide immediately before use. Eastman Kodak Co. practical grade N-methylpyrrole was also dried over Drierite and purified by fractional distillation from potassium hydroxide immediately before use. Eastman Kodak Co. practical grade pyrrole was dried over Drierite and then purified by fractional distillation at reduced pressure immediately before use. Solutions with iodine at constant initial concentration and either 2-methylfuran, furan or N-methylpyrrole, in *n*-heptane, showed isosbestic points in the region around 520 mμ indicating that iodine did not react with these donors. On the other hand, solutions of pyrrole and iodine did not show an isosbestic point and a turbid solution was produced indicating that pyrrole reacted with iodine.

Method.—The experimental method of measuring the spectra and preparing the solutions is described in a previous paper.[4] K and ϵ were calculated by using eq. 3 of this same previous paper, with suitable corrections being made for any overlapping absorption by iodine or the donor.

Results

Thiophene.—The thermodynamic and spectral characteristics of the thiophene-iodine complex are given in Tables I and II. Iodine was at a concentration of about 8×10^{-4} *M* and thiophene varied from about 0.1 to 0.5 *M* for the solutions from which the K's were calculated. At the peak of the charge-transfer band there was a very small absorption due to free thiophene and a larger, but still relatively small, absorption due to free iodine which were corrected for. In addition, it was found that when the solvent was changed from *n*-heptane to dichloromethane there

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(1) R. M. Acheson, "An Introduction to the Chemistry of Heterocyclic Compounds," Interscience Publishers, Inc., New York, N. Y., 1960.

(2) H. Tsubomura and R. P. Lang, *J. Am. Chem. Soc.*, **83**, 2085 (1961).

(3) L. J. Andrews and R. M. Keefer, *ibid.*, **74**, 4500 (1952); R. M. Keefer and L. J. Andrews, *ibid.*, **77**, 2164 (1955); J. Walkley, D. Glew and J. Hildebrand, *J. Chem. Phys.*, **33**, 621 (1960).

(4) R. P. Lang, *J. Am. Chem. Soc.*, **84**, 1185 (1962).

was a "red" shift of the charge transfer band peak from 295 to 300 mμ, which is in agreement with theory since for weak complexes the upper state of the charge transfer band is expected to be considerably more dative than the ground state.

TABLE I

THE THERMODYNAMIC CHARACTERISTICS OF THE IODINE COMPLEXES WITH THIOPHENE, 2-METHYLFURAN, FURAN AND N-METHYLPYRROLE

Donor	K, l. mole^{-1}	T, °C.	$\Delta H°$, kcal. mole^{-1}	$\Delta S°$, e.u.
Thiophene	0.44	38	-2.4 ± 0.7	-9.1 ± 1.9
	.59	20		
	.72	2		
2-Methylfuran	.29	38	-2.4 ± 0.4	-10.2 ± 1.4
	.38	20.5		
	.48	2		
Furan	.20	20.5		
N-Methylpyrrole	4.25	38	-4.5 ± 0.1	-12.6 ± 0.8
	6.50	21		
	11.4	2		

TABLE II

THE SPECTRAL CHARACTERISTICS OF THE IODINE COMPLEXES WITH THIOPHENE, 2-METHYLFURAN, FURAN, N-METHYLPYRROLE AND PYRROLE

A. The charge transfer bands

Donor	λ_{max}, mμ	ϵ_{max}, l. mole^{-1} cm.$^{-1}$	$\Delta\bar{\nu}_{1/2}$, cm.$^{-1}$	f	D (Debyes)
Thiophene	295	6,400	7600	0.21	3.6
2-Methylfuran	345	6,300	6100	0.17	3.5
	245	10,600			
Furan	317	6,400			
	~240				
N-Methylpyrrole	360	7,050			
	310	5,300			
Pyrrole	360				
	285				

B. The shifted visible iodine band

Donor	λ_{max}, mμ	ϵ_{max}, l. mole^{-1} cm.$^{-1}$
Thiophene	510	1000
2-Methylfuran	495	1200
N-Methylpyrrole	480	1200

2-Methylfuran.—In the case of 2-methylfuran the charge transfer band has a peak at about 345 mμ. For the calculation of K the concentration of iodine was about 5×10^{-4} M and 2-methylfuran varied from about 0.5 to 1.0 M. The very small absorption due to both iodine and 2-methylfuran were corrected for. The results are given in Tables I and II.

The absorption of these iodine–2-methylfuran solutions at shorter wave lengths, in the near ultraviolet, is considerably greater than can be accounted for by the sum of the absorption due to 2-methylfuran and iodine. Therefore, the absorption due to 2-methylfuran was directly subtracted from the observed absorption, and then using the calculated K the concentration of uncomplexed iodine was determined and its corresponding absorption was subtracted from this observed absorption to give another absorption band characteristic of the iodine–2-methylfuran complex. This situation is illustrated in Fig. 1. The peak of this band appears to be at 245 mμ; accurate measurements could not be made below this wave length because of the greatly increasing absorption due to 2-methylfuran and the intense contact charge-transfer absorption[5] due to uncomplexed iodine and the n-heptane solvent. The extinction coefficient of this band at 245 mμ was calculated to be about 10,600 l. mole^{-1} cm.$^{-1}$ which is substantially larger than the ϵ_{max} of the 345 mμ charge-transfer band. This 245 mμ band is probably a second charge transfer band, but some of its intensity may be due to superposition of a contact charge-transfer band due to complexed iodine and the solvent.

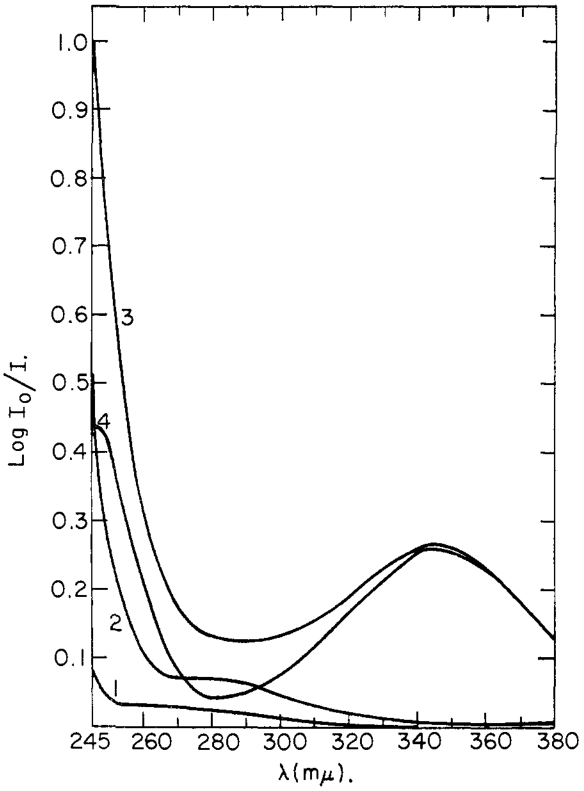

Fig. 1.—The charge transfer bands of the 2-methylfuran–iodine complex in n-heptane at 20.5° using a 1-cm. cell: curve 1, 0.222 M 2-methylfuran; curve 2, 5.28×10^{-4} M iodine; curve 3, 5.28×10^{-4} M iodine and 0.222 M 2-methylfuran; curve 4, the two charge-transfer bands of the 2-methylfuran–iodine complex.

Furan.—Solutions of furan and iodine in n-heptane were also investigated, but due to the instability and very low boiling point of furan its K was calculated only at 20.5°. These furan solutions were studied at essentially the same concentration ranges as 2-methylfuran. The results are given in Tables I and II.

Just as in the case of 2-methylfuran there was found to be a second charge-transfer band at shorter wave lengths. Measurements and calculations werre carried out to 240 mμ, but the peak of this band is at a slightly shorter wave length.

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[5] R. S. Mulliken, *Rec. trav. chim.*, **75**, 845 (1956); L. E. Orgel and R. S. Mulliken, *J. Am. Chem. Soc.*, **79**, 4839 (1957).

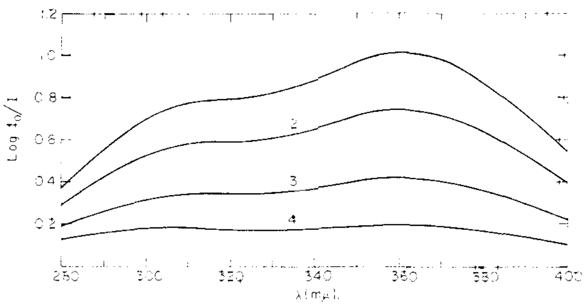

Fig. 2.—The charge transfer bands of the N-methylpyrrole–iodine complex in *n*-heptane at 21° using a 1-cm. cell: curve 1, 5.52×10^{-4} *M* iodine and 0.0537 *M* N-methylpyrrole; curve 2, 5.52×10^{-4} *M* iodine and 0.0358 *M* N-methylpyrrole; curve 3, 5.52×10^{-4} *M* iodine and 0.0179 *M* N-methylpyrrole; curve 4, 4.88×10^{-4} *M* iodine and 0.0090 *M* N-methylpyrrole.

N-Methylpyrrole.—In Fig. 2 are shown the near ultraviolet spectra of several solutions of iodine and N-methylpyrrole, in *n*-heptane, showing two charge-transfer bands. Curves 1, 2 and 3 are the spectra of three of the solutions used to calculate K while curve 4 is shown to illustrate the location of the peak of the shorter wave length band. The K was calculated from the 360 mμ peak where, at the concentrations employed, there was a very small absorption due to iodine but no absorption due to N-methylpyrrole. Table I shows that the $\Delta H°$ for the N-methylpyrrole complex is the most accurately known of those for the three complexes and that the $\Delta H°$ of the thiophene complex is the least accurately known. This is mainly because in the case of N-methylpyrrole there was the least overlapping of absorption by iodine and the donor at the peak of the charge transfer band whereas for the case of thiophene there was the greatest overlapping by iodine and the donor.

In order to determine if the shorter wave length band, with peak at 310 mμ (after correcting for absorption by iodine and the donor), belonged to the same 1:1 complex as the 360 mμ band the solution of curve 2 was cooled to 0° and then heated to about 60°. Both hands were found to be completely reversible with temperature; upon cooling, curve 2 approached curve 1 and, upon heating, curve 2 approached curve 3. Then. using the same solutions that were employed to calculate K at 360 mμ and 21° (Table I), K and $\epsilon_{\max}$ were calculated using data at 310 mμ and 21°. The resulting value of K was 6.45 l. mole^{-1} cm.$^{-1}$ and $\epsilon_{\max}$ was 5,260 l. mole^{-1} cm.$^{-1}$. These results together with the isosbestic point and the linearity of the plots of eq. 3 for both the 360 mμ and the 310 mμ data show that both bands belong to the same 1:1 molecular complex between iodine and N-methylpyrrole.

Pyrrole.—As mentioned in the Experimental section, *n*-heptane solutions of iodine and pyrrole were turbid indicating chemical reaction. However, although no accurate quantitative absorbance measurements can be made, the spectra of solutions with iodine at a concentration of about 5×10^{-4} *M* and pyrrole at about 0.05 *M* show two bands in the near ultraviolet, similar to the N-methylpyrrole case, with peaks at about 360 and 285 mμ and showing the same type of temperature reversibility as the N-methylpyrrole–iodine complex.

Discussion

As mentioned in the introduction, considerable experimental and theoretical work indicates that the compounds studied here behave, in general, like aromatic hydrocarbons. Consequently, in their basicity toward iodine one would expect these compounds to be intermediate between aromatic hydrocarbons and the corresponding n-donors. A similar case, involving a reduction in donor strength because of intramolecular resonance, is that of the N,N-dimethylaniline–iodine complex.[6] If there were no resonance between the nitrogen lone pair and the π-electrons of the aromatic ring one would expect the donor strength of this compound to be about the same as that of a tertiary amine. A comparison of the K and $\Delta H°$ of the N,N-dimethylaniline–iodine complex with those of a tertiary amine–iodine complex[7] shows a considerable reduction in donor strength, which must be attributed to the intramolecular resonance.

The $\Delta H°$ of 2-methylfuran can be compared with that of the 2-methyltetrahydrofuran–iodine complex (6.2 kcal. mole^{-1}).[8] Those of thiophene and N-methylpyrrole have to be compared with diethyl sulfide (7.8 kcal. mole^{-1})[9] and a tertiary amine (12 kcal. mole^{-1})[10] since the $\Delta H°$'s for the corresponding saturated cyclic compounds are not available. The values for the cyclic (five-membered ring) n-donors are larger than those for the corresponding open chain n-donors so that these latter two values must be regarded as lower limits.[11] Comparing these $\Delta H°$'s with those in Table I one can see that there is a considerable reduction in donor strength. A similar comparison of the K's and of the shifts of the visible iodine band indicates a large difference in donor strengths. The results of the present study, therefore, are in agreement with the generally accepted picture of the structure of these aromatic heterocyclic compounds.

Positions of the Charge Transfer Bands.—The ionization potentials[12] of thiophene, furan and 2-methylfuran are 8.9, 8.9 and 8.4 e.v., respectively, so that the positions of the charge transfer bands of the iodine complexes of these compounds are in qualitative agreement with the well-known frequency *versus* ionization potential relations.[13] The ionization potential of N-methylpyrrole is not known, whereas two widely conflicting values[14] of 8.9 and 8.2 e.v. are reported for pyrrole. The latter value is in qualitative agreement with the position of the 360 mμ band.

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[6] H. Tsubomura, *J. Am. Chem. Soc.*, **82**, 40 (1960).

[7] H. Yada, J. Tanaka and S. Nagakura, *Bull. Chem. Soc. Japan*, **33**, 1660 (1960).

[8] M. Brandon, M. Tamres and S. Searles, *J. Am. Chem. Soc.*, **82**, 2129 (1960).

[9] See ref. 2.

[10] See ref. 7.

[11] See ref. 8.

[12] K. Watanabe, T. Nakayama and J. Mottl, "Final Report on Ionization Potentials of Molecules by a Photoionization Method," University of Hawaii, Dept. of Physics, 1959, p. 37.

[13] H. McConnell, J. Ham and J. Platt, *J. Chem. Phys.*, **21**, 66 (1953); S. Hastings, J. Franklin, J. Schiller and F. Matsen, *J. Am. Chem. Soc.*, **75**, 2900 (1953).

[14] See ref. 15, p. 37.

Both the position and the intensity of the second (shorter wave length) observed electronic bands of the furan, 2-methylfuran, pyrrole and N-methylpyrrole–iodine complexes indicate that these bands are also charge transfer bands (for the anisole–iodine complex[15] two charge transfer bands have also been detected). The extinction coefficients are much too large for these bands to be perturbed bands of the donors. LCAO MO calculations[16] on thiophene, pyrrole and furan give values of 0.252β, 0.423β and 0.876β for the energy difference between the two highest filled π-molecular orbitals of these molecules. There is a qualitative agreement if one considers the longer wave length band as due to a transition involving the highest filled orbital and the shorter wave length band as involving the next highest filled orbital. Since thiophene has the two closest orbitals, one would expect the thiophene–iodine complex to have two charge transfer bands lying very close together. The fact that only one band was observed for thiophene may be due to the unresolvable superposition of two adjacent, overlapping bands; this might also explain the very high value of the half width for this band.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, HARVARD UNIVERSITY, CAMBRIDGE, MASSACHUSETTS]

The Determination of Silicon–Carbon and Silicon–Hydrogen Bond Dissociation Energies by Electron Impact[1]

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Appearance potentials of selected ions in the mass spectra of silane, tri- and tetrachlorosilane and the methyl-, ethyl-, isopropyl- and *tert*-butylsilanes and trichlorosilanes have been measured. The silicon–carbon bond dissociation energies in the organosilanes have been calculated, the results being in general higher than the carbon–carbon bond dissociation energies in the corresponding alkanes. A definite dependence on the nature of the alkyl group is observed. The silicon–hydrogen bond dissociation energies in silane and trichlorosilane are found to be 94 ± 2 and 93 ± 4 kcal. mole^{-1}, respectively. The silicon–chlorine bond dissociation energy in tetrachlorosilane is calculated to be 106 ± 4 kcal. mole^{-1}.

In common with several other areas of inorganic chemistry, silicon chemistry lacks a body of reliable and systematic thermochemical data. Indeed, only recently have consistent results been obtained for the heat of formation of silane itself.[5,6] This situation has resulted in a corresponding lack of knowledge of the strengths of bonds formed between silicon and other elements, such as carbon and hydrogen. Furthermore, only silane,[7] tetrachlorosilane,[8] tetrafluorosilane[9] and tri- and tetramethylsilane[10] have been studied by electron impact. The present investigation, involving silane, tri- and tetrachlorosilane and the series $RSiH_3$ and $RSiCl_3$, where R is methyl, ethyl, isopropyl and *tert*-butyl, represents an attempt to correct this deficiency partially. The appearance potentials reported in this paper, taken with known heats of formation and free radical ionization potentials, permit calculation of silicon–carbon and silicon–hydrogen bond dissociation energies and the heats of formation of the several silicon compounds. The ionization potentials and heats of formation of the silyl and trichlorosilyl radicals are also calculated, and an indirect evaluation of the silicon–silicon bond dissociation energy in disilane is reported.

Experimental

A sample of ethyltrichlorosilane was kindly provided by Professor E. G. Rochow, while trichloro-, tetrachloro-, and methyltrichlorosilane were commercial samples. Isopropyltrichlorosilane was prepared by treating isopropylmagnesium bromide with tetrachlorosilane in diethyl ether. These silicon compounds were purified by high vacuum distillation. *tert*-Butyltrichlorosilane was prepared by treating tetrachlorosilane with *tert*-butyllithium in *n*-pentane.[11] The volatile solid product was exhaustively purified, but a small amount of a higher molecular weight impurity remained evident in the mass spectrum.

The alkyltrichlorosilanes were cleanly reduced[12] by lithium aluminum hydride in diglyme to give the corresponding alkylsilanes in high yield. These hydrides were purified by distillation in a high vacuum system, and by gas chromatography.

The appearance potentials were measured using a Consolidated Electrodynamics Model 21-103C mass spectrometer, modified to allow magnetic scanning. Where possible the data were evaluated[13] by the separation between the linear portion of the semi-log ionization efficiency curve (normalized for 70 volt electrons) and the parallel curve from a standard material. In cases where the semi-log plots were not parallel to the standard, appearance potentials were obtained from extrapolation of voltage differences to

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[1] This research was supported by the Directorate of Chemical Sciences, Air Force Office of Scientific Research.

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