  Bull. Chem. Soc. Jpn., 61, 1335—1337 (1988)

Charge-Transfer Complexes of Nitrones. VI. Molecular Complexes of Nitrones with Iodine

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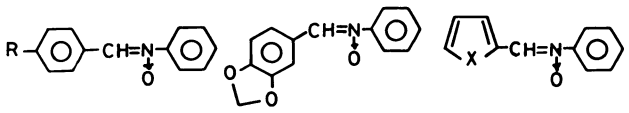
(Received April 30, 1986)

Charge-transfer (CT) complexes between some α-aryl and α-(heterocyclic substituted)nitrones and iodine as σ-acceptor in dichloromethane have been investigated spectrophotometrically. From the energies of the charge-transfer transitions, the ionization potentials of the nitrones have been obtained. The stoichiometry of the complexes has been determined. All the results are in agreement with the n-σ* nature of these complexes with some involvement of the π-orbital of the donor.

In our earlier reports,[1-4] it has been shown that nitrones form 1 : 1 CT complexes with the π-acceptors like tetracyanoethylene (TCNE), 7,7,8,8-tetracyanoquinodimethane (TCNQ), and 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ). The results indicate also that, these complexes are weak in nature and the Ph-CH=N→O moiety is responsible for the complexation with π-acceptors. Therefore, it seemed interesting to investigate the ability of nitrones to form CT complexes with σ-acceptors like iodine.

This work reports the spectrophotometric results for CT complexes of some α-aryl and α-(heterocyclic substituted) nitrones **1a—f**, **2**, and **3a,b** as donors and iodine as σ-acceptor. The role of the nitrone group, >C=N→O, as well as the aryl and heterocyclic moieties of the electron donors on the formation and stabilization of the CT complexes with iodine have been discussed. The stoichiometry and formation constant values of the different CT complexes studied have been determined. Furthermore, the ionization potentials (I.P) of the donors under investigation have been calculated.



1a—f **2** **3a, b**

1a: R = OC_2H_5; **1b**: R = OCH_3; **3a**: X = S;
1c: R = CH_3; **1d**: R = H; **3b**: X = O.
1e: R = Cl; **1f**: R = NO_2.

Fig. 1.

Experimental

E. Merck G. R. quality iodine was resublimed under reduced pressure. The nitrones **1a—f**, **2**, and **3a, b** were prepared according to the literature.[5] Dichloromethane was purified following Vogel[6] dried and distilled. The formation constants K_{ct} and the stoichiometry of the CT complexes were determined utilizing the Benesi-Hildebrand equation[7] and the conventional continuous variation method[8] (Job's method), respectively. For the purpose of determining the formation constants, the concentration of I_2 was 7.505×10^{-5} M (1M=1 mol dm^{-3}), while those of the donors **1a—f**, **2**, and **3a, b** ranged from 3×10^{-3} to 1.5×10^{-2} M. However, for the determination of the soichiometry, stock solutions (3×10^{-3} M) of donors and acceptors were prepared. The electronic spectra were recorded from 200—750 nm with a Beckman spectrophotometer model 26, using 5 cm stoppered silica cells.

Results and Discussion

A new band in the visible region (484—499 nm) is observed on mixing dichloromethane solutions of each of nitrones **1a—f**, **2**, as well as **3a, b** and iodine. This broad band is attributed to the formation of CT complexes, since neither the nitrones nor the iodine alone absorb in this region. However, after standing overnight, the violet color of the solutions varied to a more yellowish hue, and sometimes a fine brownish precipitation was produced. This behavior may be ascribed to a chemical reaction between the nitrones (reactive 1,3-dipoles) and iodine. Similar behavior was observed in the CT complexes of nitrones with the π-acceptor TCNE.[3,9]

According to the electronic structure of nitrones[10] **1a—f**, **2**, and **3a, b**, the formation of CT complexes with iodine can be attributed to either n-σ* or π-σ* interactions. In other words, n-electrons of oxygen atom of the nitrone functional group (>C=$\overset{+}{N}$-$\overline{O}$) or π-electrons of the aromatic rest can be involved in the CT complexation process. Information on this could come from the observation of the substituent effect on λ_{max} and K_{ct} of the CT complexes formed.[11] Data in Table 1 show that, the effect of different substituent on λ_{max} s and K_{ct} s is relatively small. Although there is a great difference in both inductive and mesomeric effects between the moieties which attached to the nitrone functional group, e.g. thienyl and *p*-nitrophenyl moieties, the λ_{max} values of the CT complexes lie in a narrow range (484—499 nm). In addition, a plot of transition energies of the substituted nitrones **1a—f** against the Hammett σ_p constants[12] gave a linear fit with slope (ρ)=0.42 and shows that the substituents (OC_2H_5, OCH_3, CH_3, H, Cl, and NO_2) exert weak electronic effects upon the transition energies of the CT complexes. This result indicates that, the transmission of the substituent effect in the nitrone-iodine

Table 1. Maximum Absorption Wavelengths λ_{max} (nm), Transition Energies E (kcal mol^{-1}), Molar Extinction Coefficients ε (l mol^{-1} cm^{-1}) and Formation Constants K_{ct} (l mol^{-1}) for the CT Complexes between the Nitrones **1a—f, 2,** and **3a, b** and Iodine in CH_2Cl_2 at 25 °C, as well as the Ionization Potentials I.P (eV) of the Donors **1a—f, 2,** and **3a, b**

Donor	λ_{max}/nm	E	ε	K_{ct}	I.P
		kcal mol^{-1}	l mol^{-1} cm^{-1}	l mol^{-1}	eV
1a	499	57.31	3395	23.27	6.69
1b	498	57.43	3360	22.19	6.70
1c	496	57.66	3291	21.10	6.71
3a	495	57.77	2950	21.15	6.72
2	493	58.01	3385	20.11	6.73
1d	492	58.13	3188	19.69	6.74
1e	491	58.25	2922	19.12	6.75
3b	491	58.25	2560	18.55	6.75
1f	484	59.09	2265	16.83	6.80

complexes is small and implies that the interaction between the nitrone and iodine may be ascribed to the lone pair electrons of the oxygen atom of the nitrone functional group, i.e. the n-σ^* nature of these CT complexes. On the other hand, comparison of this ρ value with the corresponding value of the analogous π-σ^* complexes[7] shows that, the nitrone **1a—f**-I_2 complexes exhibits low ρ value and give an evidence for the n-σ^* nature. Moreover, the formation constant K_{ct} values of the CT complexes (Fig. 2) follow the same pattern as λ_{max} and gives another evidence for the n-σ^* nature of the CT complexes. Hence, it can be inferred that the complexation process between the nitrones and iodine is due to the lone-pair electrons of oxygen atom. In addition, the extra negative charge on the oxygen atom should make it a better electron donor according to charge transfer theory[7,13] and consequently the center reasonably seems to be the oxygen atom. However, as was stated previously,[13] 2p π electrons of the oxygen atom in nitrones are conjugated with the rest of the π-electron system and the N-O bond has about 30% of double bond character.[14] Thus, it can be concluded that, the complexation process between the nitrones and iodine can be attributed to n-σ^* interaction, with small involvement of the π-orbital of the aromatic rest of the nitrones.

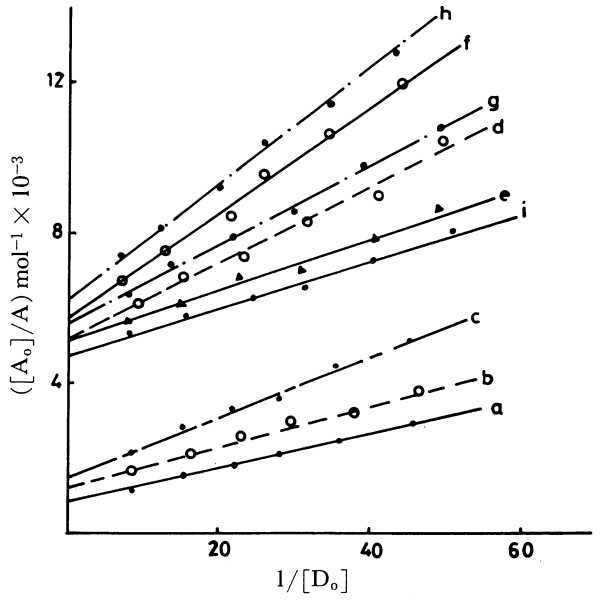


Fig. 2. Typical plots employed in the calculation of formation constants of complexes: (a) **1a**-I_2, (b) **1b**-I_2, (c) **1c**-I_2, (d) **3c**-I_2, (e) **2**-I_2, (f) **1d**-I_2, (g) **1e**-I_2, (h) **3b**-I_2, (i) **1f**-I_2; $[A_o]=7.505\times10^{-5}$ M and $[D_o]=3\times10^{-3}$ to 1.5×10^{-2} M. Dichloromethane used as solvent.

The ionization potential values listed in Table 1 were estimated from the energies of the CT bands applying the following empirical equation:[7,11]

$$\text{I.P (eV)} = 2.90 + 1.89 \times 10^{-4}\,\tilde{\nu}_{I_2}\,(\text{cm}^{-1})$$

Recently,[15] the complexation process between α-aryl nitrones and π-acceptors (TCNE and 1,4-benzoquinones) has been attributed to π-π^* interaction. A comparison of the I.P values of the nitrones **1b—e** in the case of iodine complexes with those values in cases of DDQ and TCNE complexes indicates that there is a reasonable difference between both I.P values (Table 2). Such difference suggests that the orbital of nitrones involved in the interaction with iodine acceptor is different from that involved in cases of DDQ and TCNE. Again, this result reinforces the suggestion of the n-σ^* nature of the nitrones-iodine complexes.

The stoichiometry of the molecular complexes formed were determined by application of Job's method[8] (continuous variation method). The plots of the intensity of the CT band maxima against the mole fraction of the donors (Fig. 3) furnished symmetrical curves with maxima at mole fraction 0.5 indicating

Table 2. Ionization Potentials of the Nitrones **1b—e** as obtained from Transition Energies of CT Complexes with DDQ, TCNE, and Iodine

Nitrone	I.P/eV DDQ[a]	TCNE[a]	Iodine
1b	8.02	8.07	6.70
1c	8.27	8.16	6.71
1d	8.40	8.29	6.74
1e	8.40	8.47	6.75

a) Data are taken from Ref. 16.

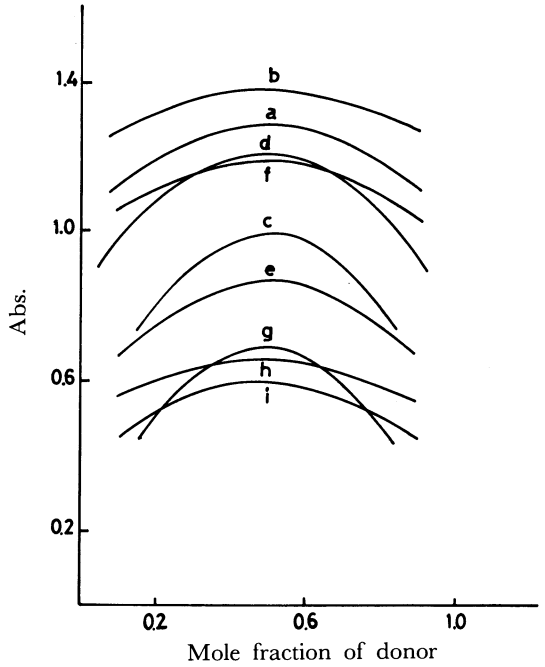


Fig. 3. Job's method for the CT complexes of I_2 with: a) **1a**; λ_{max}=499 nm, b) **1b**; λ_{max}=498 nm, c) **1c**; λ_{max}=496 nm, d) **3a**; λ_{max}=495 nm, e) **2**; λ_{max}=493 nm, f) **1d**; λ_{max}=492 nm, g) **1e**; λ_{max}=491 nm, h) **3b**; λ_{max}=491 nm, i) **1f**; λ_{max}=484 nm, total concentration=2×10^{-3} M. Dichloromethane used as solvent.

1 : 1 stoichiometric ratio for all CT complexes studied.

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