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Intensities of the T←S Transitions in Oxalyl Chloride and Bromide*[1]

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The matrix elements of the spin-orbit interaction and the intensities of the T←S transitions resulting from possible perturbing processes in glyoxal and its halogen substituted derivatives are examined. The calculated results show that the T←S transitions in these molecules borrow their intensities predominantly from the $^1B_u(\pi, \pi^*)\leftarrow{}^1A_g$ and $^3B_g(n, \pi^*)\leftarrow{}^3A_u$ transitions by means of the first-order spin-orbit interaction. An experimental study of the T←S absorptions of haloderivatives of glyoxal shows that the intensity increases with an increase in the atomic number of the halogen atom. This intensification due to halosubstitution can be interpreted in terms of two factors; (1) the halosubstitutional effects on the transition energies and on the intensities of these two perturbing transitions, and also on the transition energy of the T←S transition, and (2) the halosubstitutional effect on the matrix element of the spin-orbit interaction, which comes to involve the one-center term on the halogen atom if slight delocalizations of the *n*-orbital as well as of the π-orbital over the halogen atom are taken into account.

The intramolecular heavy-atom effects on the triplet-singlet transitions in halosubstituted aromatic hydrocarbons have been observed by several workers,[1-4] and it has been shown that heavy-atom substitution increases the T—S transition probabilities and also alters the polarization of the T→S emissions of these molecules. Recently, theoretical considerations concerning the heavy-atom effects on the phosphorescence processes in dihalonaphthalenes and halosubstituted carbonyl compounds have been made by El-Sayed.[5,6] According to his conclusions, the remarkable intramolecular heavy-atom effects observed for the $\pi^*\rightarrow\pi$ phosphorescence processes in halosubstituted aromatic hydrocarbons are mainly due to the second-order spin-orbit-vibronic interaction between the lowest (π, π^*) triplet and (π, π^*) or (σ, σ^*) singlet states; on the other hand, the heavy-atom effects on the $\pi^*\rightarrow n$ phosphorescence processes in halosubstituted carbonyl compounds are expected to be negligibly small. Recently, Carroll, Vanquickenborne and McGlynn[7] calculated the phosphorescence lifetimes for the T→S transitions in formaldehyde and some of its halogen substituents using the molecular orbitals obtained by a charge self-consistent Wolfsberg-Helmholz method and pointed out that a considerable heavy-atom effect on the phosphorescence lifetimes may be expected when one considers that the so-called *n*-orbital on the oxygen atom is mixed with carbon and halogen p-orbitals to a considerable extent.

We studied the T←S absorption spectra of haloderivatives of glyoxal and found that the intensity increases with an increase in the atomic number of the halogen atom. This paper is

*1 Submitted in partial fulfillment of the requirements for the degree of Doctor of Science of H. S., Kyushu University, 1967.

1) D. S. McClure, *J. Chem. Phys.*, **17**, 905 (1949).
2) M. S. De Groot and J. H. Van Der Waals, *Mol. Phys.*, **4**, 189 (1961).
3) T. Pavlopoulos and M. A. El-Sayed, *J. Chem. Phys.*, **41**, 1082 (1964).
4) J. K. Roy and L. Goodman, *J. Mol. Spectry.*, **19**, 389 (1966).
5) M. A. El-Sayed, *J. Chem. Phys.*, **41**, 2462 (1964).
6) M. A. El-Sayed, *ibid.*, **43**, 2864 (1965).
7) D. G. Carroll, L. G. Vanquickenborne and S. P. McGlynn, *ibid.*, **45**, 2777 (1966).

intended to investigate the possible sources of the observed intensification of the T←S transitions in oxalyl chloride and bromide.

General Considerations

In the absence of an external magnetic field, the spin-orbit interaction operator, which mixes singlet and triplet states, can be written as[8,9]:

$$H_{s.o.} = \frac{\alpha^2}{2}\sum_{\mu}\sum_{i}\frac{Z_\mu}{r^3_{i\mu}}\boldsymbol{L}_{i\mu}\cdot\boldsymbol{S}_i - \frac{\alpha^2}{2}\sum_{i\neq j}\left(\frac{\boldsymbol{r}_{ij}}{r^3_{ij}}\times\boldsymbol{P}_i\right)\cdot(\boldsymbol{S}_i+2\boldsymbol{S}_j),$$

where α is the fine structure constant*2; Z_μ is the effective nuclear charge of a nucleus, μ, on an electron, i; $\boldsymbol{L}$ and $\boldsymbol{S}$ are orbital and spin angular momentum operators respectively; $\boldsymbol{r}$ is a vector distance, and, r, its magnitude; $\boldsymbol{P}$ is a linear momentum operator; i and j refer to electrons, and μ, to nuclei, and the summations run over all nuclei and over electrons in the open shells. In the helium atom, the second term gives a greater interaction energy than the first term.[6,9] As the atomic number increases, the first term outweighs the second, and in heavy atoms it is believed that the second term can indisputably be neglected. Thus the spin-orbit interaction operator which will be used in this work can be written as:

$$H_{s.o.} = \frac{\alpha^2}{2}\sum_{\mu}\sum_{i}\frac{Z_\mu}{r^3_{i\mu}}\boldsymbol{L}_{i\mu}\cdot\boldsymbol{S}_i. \qquad (1)$$

There are three types of paths which may bring a singlet character into a triplet state: (1) the first-order spin-orbit interaction, (2) the first-order spin-vibronic interaction, and (3) the second-order spin-orbit-vibronic interaction, that is, the spin-orbit interaction with the vibronic interaction in the same manifold.[10] It has been suggested that a combination of the spin-orbit and vibronic interactions would be greater than the spin-vibronic contribution.[6,10] Thus, the oscillator strength of a T←S transition is given by:

$$f_{T_1\leftarrow S_0} = \sum_k f_{S_k\leftarrow S_0}\frac{E_{T_1}-E_{S_0}}{E_{S_k}-E_{S_0}}\left|\frac{\langle S_k|H_{s.o.}|T_1\rangle}{E_{S_k}-E_{T_1}}\right|^2 + \sum_l f_{T_l\leftarrow T_1}\frac{E_{T_1}-E_{S_0}}{E_{T_l}-E_{T_1}}\left|\frac{\langle T_l|H_{s.o.}|S_0\rangle}{E_{T_l}-E_{S_0}}\right|^2, \qquad (2)$$

where, if the intensity of a spin-allowed perturbing transition is due to a electronically-allowed transition, the perturbing mechanism corresponds to the first type while if the intensity is due to a vibronically-induced transition, the mechanism corresponds to the third type.

The matrix element of the spin-orbit interaction involving state functions can be reduced to the matrix element involving molecular orbitals; if molecular orbitals are expanded over atomic orbitals, this can be further simplified to the following:

$$\langle S_k|H_{s.o.}|T_1\rangle = \pm\frac{1}{2}\left[\frac{\alpha^2}{2}\sum_{\mu}Z_\mu\sum_{\nu}\sum_{\lambda}C_{p\nu}C_{q\lambda}\langle\chi_\nu\left|\frac{\boldsymbol{L}_\mu}{r^3_\mu}\right|\chi'_\lambda\rangle\right], \qquad (3)$$

where the factors $\pm1/2$ come from the spin-part of the matrix element, and where p and q refer to molecular orbitals and ν and λ, to atomic orbitals, χ, all of which are p-orbitals in these calculations. By considering the effect of angular momentum operators on p-orbitals, it can readily be seen that a one-center term in Eq. (3) is reduced to:

$$\pm\frac{1}{2}\frac{\alpha^2}{2}\sum_{\mu}Z_\mu C_{p\mu}C_{q\mu}\langle\chi_\mu\left|\frac{1}{r^3_\mu}\right|\chi_\mu\rangle.$$

A term without AO coefficients:

$$\frac{\alpha^2}{2}Z_\mu\langle\chi_\mu\left|\frac{1}{r^3_\mu}\right|\chi_\mu\rangle$$

will be called a one-center integral*3 hereafter; this is approximated with the spin-orbit coupling constant, ζ, of a free atom. The values which will be employed in these calculations were taken from Blume and Watson's work[11] and are given in Table 1, together with the values due to completely-unscreened nuclear charges, ζ_{nuc}. It should be noted that chlorine and bromine atoms have core electrons screening the nuclei only slightly; hence, they have large spin-orbit coupling constants.

Table 1. ζ- and ζ_{nuc}-values for carbon, oxygen, chlorine and bromine atoms (cm^{-1})*

Atom	ζ	ζ_{nuc}
Carbon	31	58
Oxygen	146	230
Chlorine	544	667
Bromine	2194	2432

* These values are taken from Ref. 11.

In calculating the spin-orbit interaction of halosubstituted carbonyl compounds, two-center terms involving a halogen atom cannot immediately be neglected without careful evaluation. El-Sayed[5] has pointed out that the two-center term in the halogen-carbon system is one of the terms

8) H. A. Bethe and E. E. Salpeter, "Quantum Mechanics of One- and Two-Electron Atoms," Springer Verlag, Berlin (1957).

9) J. C. Slater, "Quantum Theory of Atomic Structure," Vol. II, McGraw-Hill, New York (1960).

*2 Throughout this paper we use Hartree atomic units with the unit of energy of $2R_y$.

10) A. C. Albrecht, *J. Chem. Phys.*, **38**, 354 (1963).

*3 "Term" is used throughout this paper for an integral multiplied by AO coefficients.

11) M. Blume and R. E. Watson, *Proc. Roy. Soc.*, **A270**, 127 (1962).

which give rise to the observed intramolecular heavy-atom effect in halosubstituted aromatic hydrocarbons, and has estimated that when the halogen atom is iodine, the two-center term is 1—10 times larger than the term giving rise to the observed lifetime of the parent molecule.

Following the same procedure as that followed for benzene by McClure,[12] we will use the following orbital part of the operator for the calculation of two-center terms:

$$(H_{s.o.})_y' = \frac{\alpha^2}{2}\sum_{\mu}\sum_{i}\frac{Z_\mu}{r^3_{i\mu}}\left[(z-z^0{}_\mu)\frac{\partial}{\partial x} - (x-x^0{}_\mu)\frac{\partial}{\partial z}\right], \quad (4)$$

where the x axis is perpendicular to the molecular plane; the z axis, along the carbon-halogen bond; the y axis, in the molecular plane, and $z^0{}_\mu$ and $x^0{}_\mu$ are the coordinates of the nucleus, μ.*4

The evaluation of three-center terms is very complicated. The upper limit of the value of the three-center term involving the carbon atoms in benzene was estimated to be about 1 cm^{-1} by McClure.[12] El-Sayed[5] has pointed out that the three-center type halogen interaction yields matrix elements that are an order of magnitude smaller than the one-center term on the oxygen atom of the parent molecule. From these considerations, multi-center (*i. e.*, more than two-center) integrals will be neglected in these calculations.

Spin-Orbit Coupling in the Parent Molecule, Glyoxal

Since the rotational isomerism in glyoxal has hardly a pronounced influence on our conclusion, we will consider the coupling scheme on the assumption that this molecule is in the *trans*- form (C_{2h}).

Brand[13] observed a very weak absorption system in glyoxal around 5200 Å and ascribed it to a T←S transition. This assignment was affirmed by the magnetic rotation spectrum observed by Eberhardt and Renner.[14] The 0—0 band was analyzed and located at 19198 cm^{-1}. This observation definitely indicates that the T←S transition is due to a $^3A_u(n, \pi^*)\leftarrow{}^1A_g$ transition.

Nine possible perturbing processes for the T←S transition in conformity with the spin-orbit selection rules[15,16] are given in Table 2. The SCF MO's for π- and n-orbitals used in these calculations are those obtained by Sidman,[17] while the approximate MO's for σ-orbitals are similar to those used by Pople and Sidman.[18] The coordinate system is shown in Fig. 1.

As an example, we will calculate the intensity of the T←S transition contributed by the process I,

TABLE 2. POSSIBLE PROCESSES FOR PERTURBING THE T←S TRANSITION, THEIR MATRIX ELEMENTS OF THE SPIN-ORBIT INTERACTION AND INTENSITIES CONTRIBUTED FROM THESE PROCESSES IN GLYOXAL

Process	Perturbing transition: Transition	Energy, eV	f	Matrix element a u	$f_{T\leftarrow S}$
I	$^1B_u(\pi, \pi^*)\leftarrow{}^1A_g$	7.4[a]	0.3[d]	2×10^{-4}	1×10^{-7}
II	$^1B_u(n, \sigma^*)\leftarrow{}^1A_g$	7.1[b,c]	2×10^{-2} [b,c]	4×10^{-5}	9×10^{-10}
III	$^1A_u(\sigma, \pi^*)\leftarrow{}^1A_g$	10[d]	$\sim10^{-2}$ [d]	1.5×10^{-4}	1×10^{-9}
IV	$^1A_u(n_{sp}, \pi^*)\leftarrow{}^1A_g$	10[d]	$\sim10^{-2}$ [d]	2×10^{-4}	1×10^{-9}
V	$^3A_g(\pi, \pi^*)\leftarrow{}^3A_u$		very weak	no one-center	$\ll10^{-9}$
VI	$^3A_g(\sigma, \sigma^*)\leftarrow{}^3A_u$				
VII	$^3B_g(n, \pi^*)\leftarrow{}^3A_u$	$M^2=0.5$[e]		2.5×10^{-4}	3×10^{-7}
VIII	$^3B_g(\sigma, \pi^*)\leftarrow{}^3A_u$		weak	$\sim10^{-4}$	10^{-9}
IX	$^3B_g(\pi, \sigma^*)\leftarrow{}^3A_u$		very weak	$\sim10^{-4}$	10^{-9}

a) J. W. Sidman, *J. Chem. Phys.*, **27**, 429 (1957).
b) H. L. McMurry, *ibid.*, **9**, 231, 241 (1941).
c) H. Ley and B. A. Arends, *Z. Physik. Chem.*, **B12**, 132 (1931).
d) These values were assumed in this calculation.
e) M is the transition moment which was calculated in this work. Transition energy and f-value are related to M by

$$\frac{f_{^3B_g(n,\pi^*)\leftarrow{}^3A_u}}{E_{^3B_g(n,\pi^*)\leftarrow{}^3A_u}} = \text{const.} \times M^2.$$

12) D. S. McClure, *J. Chem. Phys.*, **20**, 682 (1952).
*4 This coordinate system is used only for the evaluation of two-center integrals. It should be noted that this system is different from that shown in Fig. 1.
13) J. C. D. Brand, *Trans. Faraday Soc.*, **50**, 431 (1954).
14) W. H. Eberhardt and H. Renner, *J. Mol. Spectry.*, **6**, 483 (1961).
15) D. S. McClure, *J. Chem. Phys.*, **17**, 665 (1949).
16) S. I. Weissman, *ibid.*, **18**, 232 (1950).
17) J. W. Sidman, *ibid.*, **27**, 429 (1957).
18) J. A. Pople and J. W. Sidman, *ibid.*, **27**, 1270 (1957).

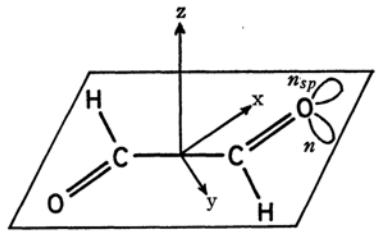

Fig. 1. Coordinate system used in the spin-orbit calculation for glyoxal.

where the ^3A_u (n, π^*) state mixes with the $^1B_u(\pi,\pi^*)$ state through S_x. The resulting matrix element involves the one-center term on the oxygen atom and was calculated to be:

$$\langle {}^1B_u(\pi, \pi^*) | H_{s.o.} | {}^3A_u(n, \pi^*) \rangle = 2 \times 10^{-4} \text{ au.}$$

The state functions employed here were:

$$^1B_u(\pi, \pi^*) = 0.980(\pi_2, \pi_3^*) + 0.189(\pi_1, \pi_4^*)$$

$$^3A_u(n, \pi^*) = 0.853(n_-, \pi_3^*) + 0.521(n_+, \pi_4^*),$$

where n_- and n_+ are:

$$n_-(a_g) = \frac{1}{\sqrt{2}}(n_O - n_{O'})$$

$$n_+(b_u) = \frac{1}{\sqrt{2}}(n_O + n_{O'}).$$

The energy of the $^1B_u(\pi, \pi^*) \leftarrow {}^1A_g$ transition is about 7.4 eV, and the f-value of this transition was assumed to be 0.3. By substituting these values into Eq. (2), the intensity of the $^3A_u(n, \pi^*) \leftarrow {}^1A_g$ transition contributed from the process I was calculated to be:

$$f_{T \leftarrow S} = 1 \times 10^{-7}.$$

The matrix elements and the intensities resulting from other processes were calculated according to a procedure similar to that described for the process I; the results are summarized in Table 2, together with the energy and the intensity of each perturbing transition.

The matrix elements which involve the one-center terms on the oxygen and/or carbon atoms were calculated to be of an order of 10^{-4} au. Thus, the relative importance in perturbing the T←S transition mainly depends on the intensities of the perturbing transitions, and it turns out that the processes I and VII can contribute the greatest intensity to the T←S transition. Indeed, the calculated results show that the process VII makes a larger contribution to the T←S transition than does the process I. This is mainly due to the smaller energy difference between the perturbing and perturbed states in the process VII than in the process I. Goodman and Krishna[19] pointed out in their work on diazines that the T←S transitions in heterocyclics with two (n, π^*) states would be strongly perturbed by a strong triplet←triplet transition between the plus and minus levels of the two (n, π^*) states; this argument is also true for glyoxal.

There is no available datum on the intensity of the T←S transition of glyoxal, but the observed intensity for diacetyl is 1.4×10^{-7}.[20] The calculated intensity of the T←S transition of glyoxal agrees well with this value.

Spin-Orbit Coupling in Oxalyl Chloride and Bromide

The most important experimental evidence regarding the nature of the T—S transitions in oxalyl chloride and bromide is the following:

(1) The T←S absorption spectra were observed in the vapor with the 0—0 bands at 4101 and 4357 Å for oxalyl chloride and bromide respectively.

(2) Their intensities are unusually strong for a multiplicity-forbidden transition. The oscillator strengths in cyclohexane at room temperature are 2.7×10^{-7} and 3.0×10^{-6} for oxalyl chloride and bromide respectively.

(3) The T→S emission of oxalyl chloride was observed in cyclohexane at 77°K, its 0—0 band being located at 4167 Å. The lifetime was 1.3×10^{-2} sec. All the bands observed in the emission spectrum could be assigned to the totally-symmetrical vibrations.

(4) The T→S emission of oxalyl bromide was too weak to be measured with our experimental apparatus.

From these facts and other spectral evidence, it was concluded that:

(1) These molecules belong to the point group C_{2h}.[21]

(2) The T—S absorption and emission spectra in these molecules are due to a $^3A_u(n, \pi^*)$—^1A_g transition.[21]

The possible perturbing processes for the $^3A_u(n, \pi^*) \leftarrow {}^1A_g$ transitions in oxalyl halides and the resulting matrix elements of the spin-orbit interaction are given in Table 3. The mixing of the p_n-orbital of a halogen atom with the p_n-orbital of the parent molecule and the mixing of both p_π-orbitals of a halogen and the parent molecule are taken into account.

It should first be mentioned that, in order to evaluate the increment of the value of the matrix elements due to the heavy-atom substitution, it is necessary only to compare the values of the resulting one- and two-center terms involving the halogen atom with the value of the one-center term on the oxygen atom given by $a_{\pi O} a_{nO} \langle$the

19) L. Goodman and V. G. Krishna, *Rev. Mod. Phys.*, **35**, 541 (1963).

20) Y. Kanda, R. Shimada and H. Shimada, to be published.

21) H. Shimada, R. Shimada and Y. Kanda, to be published.

TABLE 3. POSSIBLE PROCESSES FOR PERTURBING THE $^3A_u(n, \pi^*) \leftarrow {}^1A_g$ TRANSITIONS IN OXALYL HALIDES

Process	Perturbing transition		Matrix element
	Transition	Intensity	
I	$^1B_u(\pi, \pi^*) \leftarrow {}^1A_g$	strong	$\langle \pi \vert H_{s.o.} \vert n \rangle$
II	$^1B_u(n, \sigma^*) \leftarrow {}^1A_g$	very weak	$\langle \sigma^* \vert H_{s.o.} \vert \pi^* \rangle$
III	$^1A_u(\sigma, \pi^*) \leftarrow {}^1A_g$	weak	$\langle \sigma \vert H_{s.o.} \vert n \rangle$
IV	$^1A_u(n_{sp}, \pi^*) \leftarrow {}^1A_g$	weak	$\langle n_{sp} \vert H_{s.o.} \vert n \rangle$
V	$^3A_g(\pi, \pi^*) \leftarrow {}^3A_u$	very weak	$\langle \pi^* \vert H_{s.o.} \vert \pi \rangle$
VI	$^3A_g(\sigma, \sigma^*) \leftarrow {}^3A_u$	very weak	$\langle \sigma^* \vert H_{s.o.} \vert \sigma \rangle$
VII	$^3B_g(n, \pi^*) \leftarrow {}^3A_u$	strong	$\langle \pi^* \vert H_{s.o.} \vert n \rangle$
VIII	$^3B_g(\sigma, \pi^*) \leftarrow {}^3A_u$	very weak	$\langle \pi^* \vert H_{s.o.} \vert \sigma \rangle$
IX	$^3B_g(\pi, \sigma^*) \leftarrow {}^3A_u$	very weak	$\langle \sigma^* \vert H_{s.o.} \vert \pi \rangle$

one-center integral on the oxygen atom⟩, where $a_{\pi O}$ and a_{nO} are AO coefficients on the oxygen atom in the π- and n-orbitals respectively.

The most important two-center term in oxalyl halides arises from the matrix element of the type $\langle \sigma \vert H_{s.o.} \vert \pi \rangle$, where σ is a halogen-carbon orbital. By substituting

$$\sigma = a(2p_z)_C + b(np_z)_X + \cdots$$
$$\pi = c(2p_x)_C + d(np_x)_X + \cdots$$

and the operator, $H_{s.o.}$, given in Eq. (4) into the matrix element, one can obtain the following form of the two-center term:

$$\frac{1}{2}\frac{1}{2}\frac{\alpha^2}{2} Z_X \Bigg[(ad+bc)\Bigg(\langle (2p_z)_C \frac{1}{r^3_X} (np_z)_X \rangle + \langle (2p_x)_C \frac{1}{r^3_X} (np_x) \rangle_X \Bigg) + ad \langle (np_x)_X \frac{R}{r^3_X} \frac{\partial}{\partial x_C} (2p_z)_C \rangle - bc \langle (np_z)_X \frac{R}{r^3_X} \frac{\partial}{\partial x_C} (2p_x)_C \rangle \Bigg] + \cdots , \qquad (5)$$

where the terms multiplied by Z_C are neglected because their importance is less than that of the terms multiplied by Z_X, and where R is the distance between the carbon and halogen atoms. Four types of two-center integrals in Eq. (5), which will be here called the integrals I, II, III, and IV, are evaluated with Slater-type functions, where the effective nuclear charges are estimated from the spin-orbit coupling constants of free atoms under the central field approximation. These two-center integrals can easily be expanded in the elliptical coordinate system, and their evaluations are straightforward except for the integrals involving exponential integrals. The latter were evaluated after expansion by the τ-method,[22] and for the regions where the τ-method was invalid they were evaluated graphically. The calculated results for the carbon-chlorine, carbon-bromine, and carbon-oxygen systems are given in Table 4.

TABLE 4. CALCULATED VALUES OF THE TWO-CENTER INTEGRALS INVOLVING CARBON-OXYGEN, CARBON-CHLORINE AND CARBON-BROMINE SYSTEMS

		C-O	C-Cl	C-Br
Distance (Å)		1.2	1.72	1.84
Integral (cm^{-1})	I	7	13	13
	II	2	3	3
	III	9	15	15
	IV	10	15	15

As can be seen in Eq. (5), all two-center terms are expressed by:

$a_X a_C$⟨the two-center integral between C- and X-atoms⟩,

where a refers to an AO coefficient of an appropriate molecular orbital. These two-center terms might be able to cause an appreciable increment of the matrix element of the spin-orbit interaction only when the value of $a_X a_C$ is much larger than that of the coefficient of the one-center term on the oxygen atom, $a_{\pi O} a_{nO}$, because the values of the two-center integrals involving the carbon-bromine system are much smaller than that of the one-center integral on the oxygen atom, as can be seen in Tables 1 and 4. Unfortunately, however, this is quite unlikely; therefore, it is concluded that only the one-center term involving the halogen atom is important in the pronounced heavy-atom enhancement of the matrix element of the spin-orbit interaction.

The processes which involve the one-center term on the halogen atom are I, II, III, VII, VIII, and IX.

The perturbing transitions in the processes II and VIII have transition moment integrals of the type $\langle n \vert er \vert \sigma \rangle$, and the transition in the process IX has no transition moment in the framework of the one-electron excitation. This indicates that the intensities of these perturbing transitions

22) C. Lanczos, "Applied Analysis," Prentice Hall, Inc., Englewood Cliffs, N. J. (1956).

are very weak. It can easily be shown that the enhancement of the matrix element of the spin-orbit interaction arising from the one-center term on the halogen atom is too small to cover these very weak intensities; therefore, it may immediately be concluded that these three processes are not responsible for the observed intensification of the T←S transitions in oxalyl halides.

In the process III, the matrix element is of the type $\langle n|H_{s.o.}|\sigma\rangle$, and the resulting one-center term on the bromine atom was calculated to have a value comparable with that on the oxygen atom in the parent molecule, for only the $(p_x)_{Br}$-orbital in the σ-orbital can couple with the $(p_y)_{Br}$-orbital in the n-orbital. Although the perturbing transition in the process III may be intensified by the heavy-atom substitution, the intensity may be expected to be still weaker than that of the strong $\pi\rightarrow\pi^*$ transition which perturbs the T←S transition in the parent molecule. Therefore, it may be concluded that the heavy-atom enhancement of the matrix element of the spin-orbit interaction is, again, not sufficiently large to cover the weak intensity of the perturbing transition.

From the above considerations, it may be expected that the remaining processes, I and VII, are responsible for the observed strong intensities of the T←S transitions in oxalyl halides.

Since both processes yield the same type of matrix elements of the spin-orbit interaction, and also both give the same types of energies and transition moment integrals of the perturbing transitions, it may be expected that both processes work quite equally on the perturbation of the T←S transition. Therefore, only the process I will be discussed in detail.

First let us consider the T←S enhancement caused by halosubstitutional effects on the transition energies and the intensities involved in Eq. (2). A very strong band system, whose intensity maximum was around 1900 Å, as observed in oxalyl bromide, was ascribed to a $^1B_u(\pi, \pi^*)\leftarrow{}^1A_g$ transition.[21] On the other hand, in oxalyl chloride the corresponding band system shifts toward the shorter-wavelength side and the transition energy was assumed to be about 6.9 eV (1800 Å). We have no experimental f-values for these transitions in either molecule. The observed f-values for the first $^1A_u(n, \pi^*)\leftarrow{}^1A_g$ transitions and the molar extinction coefficients around 1850 Å in diacetyl, oxalyl chloride, and bromide are given in Table 5. Using these experimental data, and taking into consideration the general intensity enhancement caused by halosubstitution, we have assumed that the f-value of the $^1B_u(\pi, \pi^*)\leftarrow{}^1A_g$ transition of oxalyl chloride is slightly larger, and that of oxalyl bromide is about twice or three times larger, than that of glyoxal. When these values and the energies of the T←S transitions given in Table 5 were substituted into Eq. (2), it was made clear that these halosubstitutional effects cause twice and four or five times larger $f_{T\leftarrow S}$-values than that of glyoxal on oxalyl chloride and bromide respectively.

Next let us consider the heavy-atom enhancement of the matrix element of the spin-orbit interaction.

Table 5. Observed f-values of the $^1A_u(n, \pi^*)\leftarrow{}^1A_g$ transitions, molar extinction coefficients around 1850 Å and energies of the $^3A_u(n, \pi^*)\leftarrow{}^1A_g$ transitions for glyoxal, diacetyl, oxalyl chloride and bromide

Molecule	$f_{^1A_u(n,\pi^*)\leftarrow{}^1A_g}$	$\varepsilon_{1850\,Å}$	$E_{^3A_u(n,\pi^*)\leftarrow{}^1A_g}$, eV
Glyoxal			2.38*
Diacetyl	3.4×10^{-4}	1700	2.45
Oxalyl chloride	4.3×10^{-4}	2500	3.00
Oxalyl bromide	7.0×10^{-4}	12000	2.85

* Taken from Ref. 13.

Table 6. π-MO's of oxalyl chloride and bromide and values of parameters used in this calculation

Molecule	MO	Coefficient						Parameter			
		(O_1+O_2)	(O_1-O_2)	(C_1+C_2)	(C_1-C_2)	(X_1+X_2)	(X_1-X_2)	$\delta\alpha_C$	β_{CX}	S_{CX}	I_X
Oxalyl chloride	π_1	0.472		0.512		0.094		eV	eV		eV
	π_2		0.525		0.413		0.134	−0.72	−1.9	0.13	−12.8
	π_3	−0.519		0.478		−0.073					
	π_4		−0.416		0.569		−0.102				
Oxalyl bromide	π_1	0.480		0.516		0.051					
	π_2		0.498		0.361		−0.349	−0.6	−1.9	0.13	−12.0
	π_3	−0.514		0.478		−0.077					
	π_4		−0.413		0.570		−0.088				

The main part of the matrix element in the process I is expressed by $\langle n_- | H_{s.o.} | \pi_2 \rangle$, which yields the following one-center terms on the carbon, halogen, and oxygen atoms:

$a_{\pi C} a_{nC} \langle$one-center integral on the C-atom$\rangle$

$a_{\pi X} a_{nX} \langle$one-center integral on the X-atom$\rangle$

$a_{\pi O} a_{nO} \langle$one-center inetgral on the O-atom$\rangle$,

where the a's are AO coefficients. The one-center term on the carbon atom is unimportant for the heavy-atom enhancement. The π-MO's of oxalyl halides were calculated by the perturbation theory[23]; these are given in Table 6, together with the parameters used in these calculations. This table shows that the AO coefficients on the chlorine and bromine atoms are about one-third and two-thirds, respectively, of that on the oxygen atom in the π_2-orbital. Let us assume tentatively that the n-electron is distributed over the atoms in the following manner:

O-atom: 90%, X-atom: 5%, C-atom: 5%.

This corresponds to the assumption that the AO coefficient on the halogen atom is about a quarter of that on the oxygen atom in the n-orbital. Substituting these AO coefficients and the one-center integrals given in Table 1 into the above expressions, one obtains:

$$\frac{\text{one-center term on the Cl-atom}}{\text{one-center term on the O-atom}} = \frac{1}{3} \times \frac{1}{4} \times \frac{544}{146} \approx \frac{1}{3}$$

$$\frac{\text{one-center term on the Br-atom}}{\text{one-center term on the O-atom}} = \frac{2}{3} \times \frac{1}{4} \times \frac{2194}{146} \approx 2.5 .$$

These results indicate that a bromine atom enhances the matrix element of the spin-orbit interaction about twice or three times as much as glyoxal, while a chlorine atom produces no pronounced enhancement for oxalyl chloride.

Taking into account both the origins of the heavy-atom enhancement described above, the intensities of the T←S transitions in oxalyl chloride and bromide are calculated to be about twice and about twenty times, respectively, larger than that in glyoxal; these results agree quite well with the experimental findings.

Although the assumption made concerning the distribution of the n-electron is quite arbitrary and the distribution of the π-electrons is obtained only by simple calculations, it can be stated that the charge densities of n- and π-electrons on the bromine atom are distributed in such a way that the one-center term on the bromine atom contributes a value to the matrix element of the spin-orbit interaction about twice that of the one-center term on the oxygen atom.

Conclusion

The T←S transitions of oxalyl halides, and also of glyoxal, are predominantly perturbed by the $^1B_u(\pi, \pi^*) \leftarrow {}^1A_g$ and $^3B_g(n, \pi^*) \leftarrow {}^3A_u$ transitions through the first-order spin-orbit interaction. The observed enhancement of the T←S transitions in oxalyl halides is caused by two factors: (1) the halo-substitutional effects on the energies and the intensities of the perturbing transitions and on the energies of the T←S transitions, and (2) the halosubstitutional effect on the matrix element of the spin-orbit interaction. The observed T←S intensification in oxalyl chloride can well be interpreted only by the first factor, and that in oxalyl bromide, by both the factors. The first factor causes only about four or five times larger $f_{T\leftarrow S}$-value than that of glyoxal on oxalyl bromide; therefore, the remaining intensification must arise from the second factor. This requires that the charge densities of π- and n-electrons on the bromine atom are distributed in such a way that the one-center term on the bromine atom can contribute a value to the matrix element of the spin-orbit interaction about twice as large as that on the oxygen atom. Within the framework of our approximations, it is necessary that only about five percent of the n-electron is distributed on the bromine atom. In this way, one can prove directly the delocalization of an n-electron, although this delocalization may be so little that one has not yet been able to detect it directly by other spectroscopic techniques.

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