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## 146. The Competition between Spin Orbit Coupling and Conjugation in Alkyl Halides and its Repercussion on their Photoelectron Spectra<sup>1)</sup>

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(17. V. 71)

*Summary.* A crude molecular orbital model for alkyl halides is proposed, which provides a semi-quantitative rationalization for the following experimental observations: (a) In the photoelectron spectra of alkyl halides RX (symmetry  $C_s$ ) the lone pair band is split into two components, separated by a gap  $\Delta$ . This gap is equal to the splitting associated with spin-orbit coupling in systems where X lies on a symmetry axis of order  $n \geq 3$ . (b) The vibrational pattern of the two components indicates substantial conjugation between R and X. (c) Notwithstanding (b), the gap  $\Delta$  is largely independent of the type of alkyl group R. (d) For strongly conjugating alkyl groups (*e.g.* R = cyclopropyl) the first component of the lone pair band (*i.e.* the one at lower ionization potential) broadens while the one at higher potential sharpens up.

Consider a halide molecule RX (X = halogen atom) in which the bond R-X coincides with an  $n$ -fold axis of the system ( $n \geq 3$ ). Photoejection



of an electron  $e$  from a  $\pi$ -type "lone pair" orbital of X yields the radical cation  $RX^+$  in a doublet spin state. Because of spin-orbit coupling this  $^2II$  term is split into two levels,  $^2II_{3/2}$  and  $^2II_{1/2}$ , which differ in energy by

$$\varepsilon(^2II_{3/2}) - \varepsilon(^2II_{1/2}) = -\zeta(X), \quad (2)$$

<sup>1)</sup> Part 25 of 'Applications of Photoelectron Spectroscopy'. Part 24: [1].

the level with total angular momentum  $\Omega = 3/2$  being more stable than the one with  $\Omega = 1/2$  (inversion). (By convention the interval (2) is then defined as a negative quantity.)

For a single electron moving in a central field with potential  $V(\varrho) = -Ze^2/\varrho$  the interaction parameter  $\zeta$  is predicted to increase with  $Z^4$  [2], but in many-electron atoms  $\zeta$  is found experimentally to be roughly proportional to  $Z^2$ , e.g.  $\zeta(\text{C}) = 0.004$  eV [3];  $\zeta(\text{F}) = 0.033$  eV;  $\zeta(\text{Cl}) = 0.073$  eV;  $\zeta(\text{Br}) = 0.305$  eV;  $\zeta(\text{I}) = 0.628$  eV. (The  $\zeta(\text{X})$  values of the halogen atoms are calculated according to  $\varepsilon(^2P_{3/2}) - \varepsilon(^2P_{1/2}) = -3 \zeta(\text{X})/2$  from the data given in [4]).

If the  $\pi$ -type "lone pair" orbital  $\psi_\lambda$  (angular momentum quantum number  $\lambda = +1$  or  $-1$ ) vacated in the course of process (1) is centered entirely on the halogen atom X of RX, i.e. if  $\psi_\lambda = n\mathbf{p}_\lambda(\text{X})$ , then we should expect, according to (2), that the corresponding PE.-band in the photoelectron spectrum of RX is split into two components (corresponding to the levels  $^2\Pi_{3/2}$  and  $^2\Pi_{1/2}$ ) by an amount

$$\Delta = I_{v, 3/2} - I_{v, 1/2} = -\zeta(\text{X}) \quad (3)$$

( $I_{v, 3/2}$  and  $I_{v, 1/2}$  are the vertical ionization potentials of the two components of the split  $^2\Pi$ -PE.-band.) For X = Br and X = I the expectation values of  $\Delta$  are therefore  $\Delta = -0.31$  eV and  $\Delta = -0.63$  eV respectively. This is indeed what has been observed; e.g. HBr:  $\Delta = -0.32$  eV, HI:  $\Delta = -0.66$  eV [5];  $\text{CH}_3\text{Br}$ :  $\Delta = -0.32$  eV;  $\text{CH}_3\text{I}$ :  $\Delta = -0.62$  eV [6]. (See also [7].)

If, on the other hand, the  $\pi$ -type "lone pair" orbitals  $\psi_\lambda$  are not strictly localized on X, but have to be written (in ZDO approximation) as linear combinations

$$\psi_\lambda = c_X \cdot n\mathbf{p}_\lambda(\text{X}) + \sum_{\mu \neq \text{X}} c_\mu \phi_\lambda(\mu) \quad (4)$$

( $\phi_\lambda(\mu)$  = basis atomic orbitals of  $\pi$ -type localized in R), then the interval (2) and thus the split (3) should be given by

$$\zeta = c_X^2 \zeta(\text{X}) + \sum_{\mu \neq \text{X}} c_\mu^2 \zeta(\mu). \quad (5)$$

In (5)  $\zeta(\mu)$  is the interaction parameter for an electron moving in orbital  $\phi_\lambda(\mu)$  of atom  $\mu$ .

Relative to the limiting case  $\psi_\lambda \equiv n\mathbf{p}_\lambda(\text{X})$  ( $c_X = 1$ ;  $c_\mu = 0$ ) discussed above, which leads to  $\zeta = \zeta(\text{X})$ , mixing of  $n\mathbf{p}_\lambda(\text{X})$  with other  $\pi$ -type orbitals  $\phi_\lambda(\mu)$  of R will necessarily result in a decrease of  $\zeta$ , if R consists of second row elements only, because  $\zeta(\mu) \ll \zeta(\text{X})$ . As a consequence, the split  $\Delta = -\zeta$  between the two components of the PE.-band which corresponds to a  $^2\Pi$ -term generated by ejecting an electron from  $\psi_\lambda$  should be a sensitive probe for the relative participation of the atomic orbitals  $n\mathbf{p}_\lambda(\text{X})$  and of the  $\pi$ -type orbitals  $\phi_\lambda(\mu)$  of R in the "lone pair" linear combination  $\psi_\lambda$ . Examples for such a dependence of  $\Delta$  on the amount of mixing between  $n\mathbf{p}_\lambda(\text{X})$  and  $\phi_\lambda(\mu)$  have been given in previous communications for the dihaloacetylenes [7], the cyanohalides [8] and the haloacetylenes [9].

We shall now turn to the alkyl halides RX (R =  $\text{C}_r\text{H}_s$ ). We exclude highly symmetrical cases, such as R =  $\text{CH}_3$ , *t*-butyl, 4-bicyclo[2.2.2]octyl etc., and assume that RX belongs to the symmetry group  $C_s$ .

If the lone pair atomic orbitals  $\mathbf{np}_\lambda$  of X do *not* conjugate at all with orbitals of R, then the electrons occupying  $\mathbf{np}_\lambda$  will feel only the cylindrically symmetrical local field. As a consequence spin orbit coupling will be the same as in a molecule RX possessing an axis of order  $n \geq 3$ , and having  $\pi$ -type lone pair orbitals  $\mathbf{np}_\lambda(X)$  completely localized on X.

On the other hand conjugative interaction among X and R should have mainly two effects:

1) The spin orbit coupling parameter  $\zeta$  and thus the split  $\Delta$  (see (3)) will decrease due to the delocalization effect described above.

2) As the semilocalized molecular orbitals  $\varphi_i$  of R must be either symmetrical or antisymmetrical with respect to the plane of symmetry of RX, their interaction with the localized atomic orbitals of X will mix  $\mathbf{np}_{+1}(X)$  with  $\mathbf{np}_{-1}(X)$ . This will again lead to a reduction of spin orbit coupling (and thus of  $\Delta$ ), as becomes obvious by considering the limiting case where the lone pair atomic orbitals have degenerated to the pair  $\mathbf{np}_x(X)$  and  $\mathbf{np}_y(X)$ .

However, the presence of these two effects does not imply that we should observe a single, unsplit "lone pair" band in the PE.-spectrum of RX: Even for the limiting case ( $\mathbf{np}_{+1}(X)$ ,  $\mathbf{np}_{-1}(X) \rightarrow \mathbf{np}_x(X)$ ,  $\mathbf{np}_y(X)$ ) we still expect a sizeable split  $\Delta$  between the PE.-bands to be assigned to the two mixed "lone pair" orbitals of X because of the difference in interaction of  $\mathbf{np}_x(X)$  and of  $\mathbf{np}_y(X)$  with the semilocalized orbitals  $\varphi_i$  of R belonging to the appropriate irreducible representations.

Keeping this in mind, it is rather unexpected that the "lone pair" PE.-band in the PE.-spectra of alkyl bromides RBr and alkyl iodides RI which belong to the symmetry group  $C_s$  is still split into two components separated within the limits of experimental error by the full values  $\zeta(\text{Br}) = 0.3$  eV and  $\zeta(\text{I}) = 0.6$  eV, largely independent of the size and type of the alkyl group R [10] as shown in tab. 1. (For a

Table 1. Ionization potentials of alkyl halides RX

$I(n)_1$  and  $I(n)_2$  are both the vertical and the adiabatic ionisation potentials of the two components of the "lone pair" bands.  $\overline{I(n)} = (I(n)_1 + I(n)_2)/2$ ;  $\Delta(n) = I(n)_1 - I(n)_2$ . All values in eV.

R	X = Br				X = I			
	$I(n)_1$	$I(n)_2$	$\overline{I(n)}$	$-\Delta(n)$	$I(n)_1$	$I(n)_2$	$\overline{I(n)}$	$-\Delta(n)$
$\text{CH}_3-$	10.53	10.85	10.69	0.32	9.52	10.14	9.83	0.62
$\text{CH}_3\text{CH}_2-$	10.30	10.61	10.46	0.31	9.35	9.93	9.64	0.58
$\text{CH}_3\text{CH}_2\text{CH}_2-$	10.18	10.49	10.34	0.31	9.25	9.83	9.54	0.58
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2-$	10.13	10.44	10.29	0.31	9.23	9.81	9.52	0.58
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2-$	10.09	10.40	10.25	0.31	9.22	9.78	9.50	0.56
$(\text{CH}_3)_2\text{CH}-$	10.12	10.41	10.27	0.29	9.19	9.75	9.47	0.56
$(\text{CH}_3)_3\text{C}-$	9.95	10.24	10.09	0.29	9.08	9.64	9.36	0.56

notable exception, see below.) On the other hand the mean of the vertical ionization potentials associated with the two components does depend markedly on the size and type of R [10], [11] (see tab. 1). This might suggest that the influence of R is strictly polar and that the vacated orbitals are completely localized on the halogen atom X. If this were indeed the case, then PE.-spectroscopy would be the ideal tool

for the assessment of polar parameters of the  $\sigma^*$ -type [12] to be used in linear free energy relationships involving alkyl groups [13].

However, this explanation cannot be true. As already mentioned by *Cocksey, Eland & Danby* [11], the two components of the lone pair band in the PE.-spectra of RX possess a vibrational fine-structure which clearly indicates that there must be an appreciable conjugative interaction with the alkyl moiety. This interaction increases in intensity and also in complexity with increasing size of the alkyl group, as shown in the examples given in fig. 1. Furthermore, cyclopropyl bromide [10] [14] (and to a lesser degree cyclobutyl bromide [15]) yields a PE.-spectrum in which the *first* component (*i.e.* the one at lower ionization potential) has degenerated into a wide fine-structured band. There is hardly any doubt that this is due to the strong preferential conjugation of one of the lone pair orbitals (say  $n\mathbf{p}_x(\text{Br})$ ) with the *Walsh*-orbital [16], of appropriate symmetry of the cycloalkyl group.

The aim of this note is to provide an explanation for the following, seemingly conflicting observations, namely:

a) that the split  $\Delta(X)$  between the two components of the “lone pair” band in the PE.-spectrum of an alkyl halide RX of low symmetry (*e.g.*  $C_s$ ) has the full value of the spin orbit interaction parameter  $\zeta(X)$ ,

b) that this split  $\Delta(X)$  is independent of the nature of the alkyl group R even though the conjugative interaction with R varies considerably as shown by the vibrational fine structure of the two components of the “lone pair” band,

c) that for increasing conjugative interaction (*i.e.* R = cyclopropyl or cyclobutyl) the shape of the component at *lower* ionization potential broadens markedly while the one at *higher* potential remains sharp (see fig. 1).

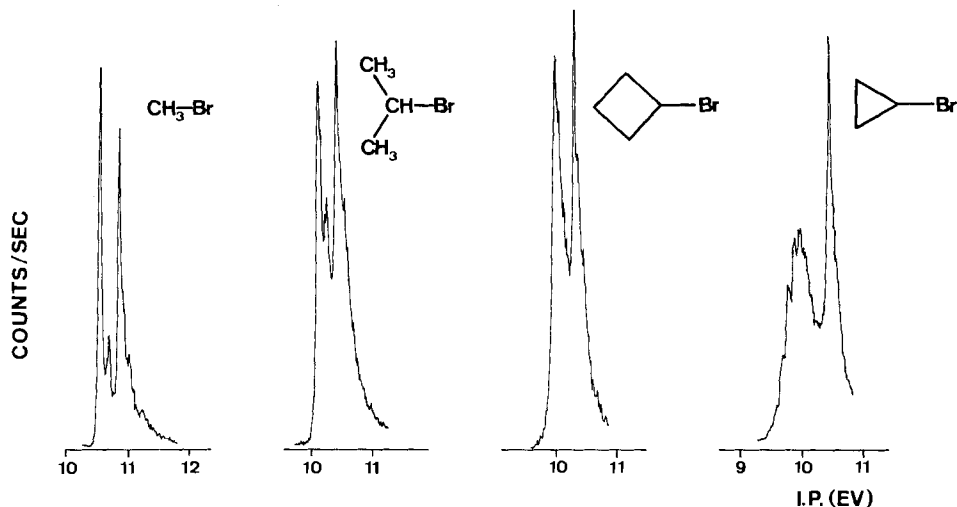
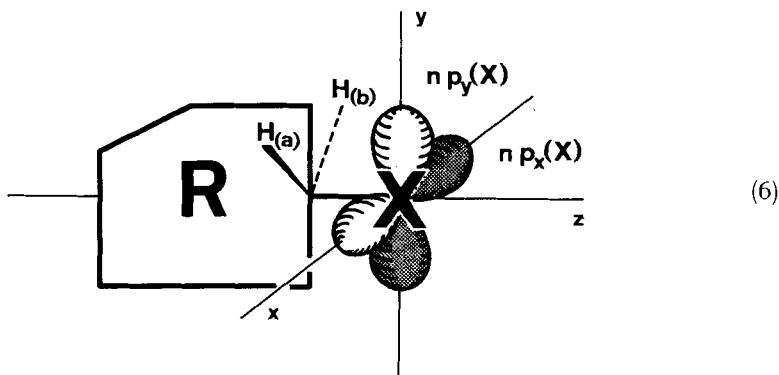


Fig. 1. “Lone pair” bands in the PE.-spectra of methyl bromide, isopropyl bromide, cyclobutyl bromide and cyclopropyl bromide

These observations can be satisfactorily reproduced by a many-electron treatment. However, the results so obtained are mimicked reasonably well by a simple one-

electron orbital model, which has the advantage of yielding a heuristically useful insight into the problem for those who are accustomed to think in terms of orbitals.

We assume that our molecule  $RX$  has  $C_s$  symmetry and define the coordinate system and the  $np(X)$  basis functions as follows:



Let  $\sigma(z y)$  be the plane of symmetry. We shall make the arbitrary assumption that conjugation between  $R$  and  $X$  will involve only  $np_x(X)$  of  $X$  and a single orbital  $\varphi(R)$  of  $R$ , both of which belong to the irreducible representation  $A''$  of  $C_s$ .

In a more complete treatment the whole set of semilocalized basis orbitals  $\varphi_i(A'')$  of  $R$  will interact with  $np_x(X)$  and the set  $\varphi_j(A')$  with  $np_y(X)$ , the magnitude of the interactions being necessarily different for the two sets. Our simplifying assumption implies that the set of orbitals  $\varphi_i(A'')$  is reasonably well represented, in a first approximation, by a single orbital  $\varphi(R)$  and that its interaction with  $np_x(X)$  is so much larger than the one between  $np_y(X)$  and the set  $\varphi_j(A')$  that the latter interaction can be neglected.

The *Hückel* orbitals for our model system (6) are therefore given in zero differential overlap (ZDO) approximation by

$$\psi = c_x np_x(X) + c_y np_y(X) + c_\varphi \varphi(R), \quad (7)$$

all basis functions being normalized. The corresponding hamiltonian is

$$\mathcal{H}' = \mathcal{H} + \mathcal{H}_{\text{soc}} \quad (8)$$

where  $\mathcal{H}$  is the usual HMO operator defined by the following list of matrix elements:

$$\begin{aligned} \langle np_x(X) | \mathcal{H} | np_x(X) \rangle &= \langle np_y(X) | \mathcal{H} | np_y(X) \rangle = \varepsilon_p(X) \\ \langle \varphi(R) | \mathcal{H} | \varphi(R) \rangle &= \varepsilon_\varphi(R) \\ \langle np_x(X) | \mathcal{H} | np_y(X) \rangle &= \langle \varphi(R) | \mathcal{H} | np_y(X) \rangle = 0 \\ \langle np_x(X) | \mathcal{H} | \varphi(R) \rangle &= \beta \end{aligned} \quad (9)$$

The spin orbit coupling operator  $\mathcal{H}_{\text{soc}}$  is arbitrarily defined in such a way that it yields an orbital sequence which reproduces the correct ordering of  ${}^2I_{\Omega}$  levels in the absence of conjugation between  $R$  and  $X$ , (*i.e.* with inversion:  $\varepsilon({}^2I_{3/2}) < \varepsilon({}^2I_{1/2})$ ) if we apply *Koopmans'* theorem [17], under the *ad hoc* assumption that the ejected electron has  $\beta$  spin (*i.e.*  $s_z = -\hbar/2$ ). (Note that the use of the correct spin orbit

coupling operator (see [2] [3]) would yield the inverse order ( $\varepsilon(^2\Pi_{1/2}) < \varepsilon(^2\Pi_{3/2})$ ) if applied to our one electron model.) Accordingly we postulate:

$$\begin{aligned}\langle n\mathbf{p}_{+1}(X) | \mathcal{H}_{\text{SOC}} | n\mathbf{p}_{+1}(X) \rangle &= \zeta(X)/2 \\ \langle n\mathbf{p}_{-1}(X) | \mathcal{H}_{\text{SOC}} | n\mathbf{p}_{-1}(X) \rangle &= -\zeta(X)/2 \\ \langle n\mathbf{p}_{-1}(X) | \mathcal{H}_{\text{SOC}} | n\mathbf{p}_{+1}(X) \rangle &= 0\end{aligned}\quad (10)$$

As the complex atomic orbitals used in (10) are [2] ( $i \equiv \sqrt{-1}$ )

$$\begin{aligned}n\mathbf{p}_{+1}(X) &= (1/\sqrt{2}) (n\mathbf{p}_x(X) + i \cdot n\mathbf{p}_y(X)) \\ n\mathbf{p}_{-1}(X) &= (1/\sqrt{2}) (n\mathbf{p}_x(X) - i \cdot n\mathbf{p}_y(X))\end{aligned}\quad (11)$$

we obtain from (10) and (11) the following matrix elements:

$$\begin{aligned}\langle n\mathbf{p}_x(X) | \mathcal{H}_{\text{SOC}} | n\mathbf{p}_x(X) \rangle &= \langle n\mathbf{p}_y(X) | \mathcal{H}_{\text{SOC}} | n\mathbf{p}_y(X) \rangle = 0 \\ \langle n\mathbf{p}_x(X) | \mathcal{H}_{\text{SOC}} | n\mathbf{p}_y(X) \rangle &= -i\zeta(X)/2 \\ \langle n\mathbf{p}_y(X) | \mathcal{H}_{\text{SOC}} | n\mathbf{p}_x(X) \rangle &= i\zeta(X)/2\end{aligned}\quad (12)$$

Consequently the secular determinant corresponding to the MO model defined by (7) and (8) is:

$$\begin{vmatrix} \varepsilon_p(X) - \varepsilon & -i\zeta(X)/2 & \beta \\ i\zeta(X)/2 & \varepsilon_p(X) - \varepsilon & 0 \\ \beta & 0 & \varepsilon_\varphi(R) - \varepsilon \end{vmatrix} = 0\quad (13)$$

We consider first two limiting cases.

A)  $\beta = 0$ .

Solution of (13) yields the orbital energies and the linear combinations

$$\begin{aligned}\varepsilon_1 &= \varepsilon_p(X) + \zeta(X)/2; & \psi_1 &= n\mathbf{p}_{+1}(X) \\ \varepsilon_2 &= \varepsilon_p(X) - \zeta(X)/2; & \psi_2 &= n\mathbf{p}_{-1}(X) \\ \varepsilon_3 &= \varepsilon_\varphi(R); & \psi_3 &= \varphi(R)\end{aligned}\quad (14)$$

where  $\psi_1$  and  $\psi_2$  are as given in (11).

B)  $\beta \gg \zeta(X)$ .

In this case we find, setting  $\bar{\varepsilon} = (\varepsilon_p(X) + \varepsilon_\varphi(R))/2$  and  $\delta = (\varepsilon_p(X) - \varepsilon_\varphi(R))/2$ :

$$\begin{aligned}\varepsilon_1 &= \bar{\varepsilon} + \sqrt{\delta^2 + \beta^2} \approx \bar{\varepsilon} + |\beta|; & \psi_1 &\approx (1/\sqrt{2}) (n\mathbf{p}_x(X) - \varphi(R)) \\ \varepsilon_2 &\approx \varepsilon_p(X); & \psi_2 &\approx n\mathbf{p}_y(X) \\ \varepsilon_3 &= \bar{\varepsilon} - \sqrt{\delta^2 + \beta^2} \approx \bar{\varepsilon} - |\beta|; & \psi_3 &\approx (1/\sqrt{2}) (\varphi(R) + n\mathbf{p}_x(X))\end{aligned}\quad (15)$$

The behaviour of the orbital energies for intermediate values of  $\beta$  is shown in fig. 2 for the particular case of RBr with  $\zeta(\text{Br}) = 0.3$  eV and  $\varepsilon_p(\text{Br}) - \varepsilon_\varphi(\text{R}) = 1.0$  eV. The remarkable result is that for  $\beta$  in the interval  $0 \leq \beta < 0.35$  eV, the gap  $\varepsilon_1 - \varepsilon_2$

Table 2. *Computed orbital energies  $\epsilon_1, \epsilon_2$  for the MO-model (6) with  $X = Br$* 

 All values in eV. Reference energy  $\epsilon_p(Br) = 0$ .  $\zeta(Br) = .30$  eV;  $\bar{\epsilon} = (\epsilon_1 + \epsilon_2)/2$ ;  $\Delta_{12} = \epsilon_1 - \epsilon_2$ .

$\epsilon_p(Br) - \epsilon_p(R)$	$\beta = 0.0$ eV				$\beta = -.1$ eV				$\beta = -.2$ eV			
	$\epsilon_1$	$\epsilon_2$	$\bar{\epsilon}$	$\Delta_{12}$	$\epsilon_1$	$\epsilon_2$	$\bar{\epsilon}$	$\Delta_{12}$	$\epsilon_1$	$\epsilon_2$	$\bar{\epsilon}$	$\Delta_{12}$
.5 eV	.1500	-.1500	.0000	.3000	.1578	-.1369	.0105	.2947	.1822	-.1075	.0374	.2897
1.0 eV	.1500	-.1500	.0000	.3000	.1544	-.1443	.0051	.2987	.1681	-.1288	.0197	.2969
1.5 eV	.1500	-.1500	.0000	.3000	.1531	-.1464	.0034	.2994	.1625	-.1361	.0132	.2986
2.0 eV	.1500	-.1500	.0000	.3000	.1523	-.1473	.0025	.2997	.1596	-.1396	.010	.2992
2.5 eV	.1500	-.1500	.0000	.3000	.1519	-.1479	.0020	.2998	.1577	-.1418	.008	.2995
$\epsilon_p(Br) - \epsilon_p(R)$	$\beta = -.3$ eV				$\beta = -.4$ eV				$\beta = -.5$ eV			
	$\epsilon_1$	$\epsilon_2$	$\bar{\epsilon}$	$\Delta_{12}$	$\epsilon_1$	$\epsilon_2$	$\bar{\epsilon}$	$\Delta_{12}$	$\epsilon_1$	$\epsilon_2$	$\bar{\epsilon}$	$\Delta_{12}$
.5	.2245	-.0775	.0735	.3020	.2836	-.0544	.1146	.3380	.3555	-.0387	.1584	.3942
1.0	.1924	-.1078	.0423	.3002	.2286	-.0861	.0713	.3148	.2770	-.0671	.105	.3441
1.5	.1792	-.1209	.0292	.3001	.2041	-.1033	.0504	.3074	.2383	-.0857	.076	.3240
2.0	.1721	-.1279	.0221	.3000	.1909	-.1135	.0387	.3044	.2166	-.0980	.0593	.3146
2.5	.1678	-.1322	.0178	.3000	.1828	-.1201	.0313	.3029	.2032	-.1066	.0483	.3098

between the two upper orbitals  $\psi_1$  and  $\psi_2$  does not change by more than one per cent. (See also tab. 2 where the results are given for  $\epsilon_p(Br) - \epsilon_p(R)$  in the range 0.5 to 2.5 eV.) The (obvious) reason for this behaviour is that for small values of  $\beta$  the orbital  $\varphi(R)$  has a slightly stronger second order interaction with  $np_{-1}(X)$  than with  $np_{+1}(X)$ , which tends to reduce the gap  $\epsilon_1 - \epsilon_2$ . However, with increasing size of  $\beta$  the conjugation tends to mix  $np_{+1}(X)$  and  $np_{-1}(X)$  until, in the limit  $|\beta| \rightarrow \infty$ ,  $\psi_2$  turns into  $np_y(X)$  whose energy  $\epsilon_2 = \epsilon_p(X)$  becomes independent of  $\beta$ . On the other hand, the strong interaction among  $\varphi(R)$  and  $np_x(X)$  raises the orbital energy  $\epsilon_1$ , which leads to an increase in the difference  $\Delta_{12} = \epsilon_1 - \epsilon_2$ . In the interval specified the two opposite trends compensate, so that the original gap  $\Delta(X) = -\zeta(X)$  observed for  $\beta = 0$  is conserved within narrow limits.

It should be noted that in a more elaborate model we should consider the competitive influence on  $\Delta_{12}$  of the conjugative interaction of both  $np_x(X)$  and  $np_y(X)$  with the two sets of semi-localized orbitals  $\varphi_i(A'')$  and  $\varphi_j(A')$  of R respectively. However, this would not change the qualitative conclusions derived above.

We now discuss the influence of conjugation on the mean orbital energy  $\bar{\epsilon} = (\epsilon_1 + \epsilon_2)/2$  and on the vibrational fine structure of the "lone pair" bands.

As seen from tab. 2, the conjugative interaction of R with X raises the mean orbital energy  $\bar{\epsilon}$ , corresponding to a reduction of the mean ionization potential  $I_v$ . In the particular case of  $\epsilon_p(Br) - \epsilon_p(R) = 1.0$  eV and  $\beta = 0.3$  eV the displacement amounts to approximately 0.04 eV and except for extreme cases ( $|\beta| > 0.4$  eV) it is always smaller than  $\sim 0.1$  eV. It is evident that for larger values of  $\beta$  and/or smaller gaps  $\epsilon_p(X) - \epsilon_p(R)$  this displacement would have to be taken into consideration before converting the observed shift values into parameters assumed to be representative solely for the polar effects of R.

We have mentioned that conjugation between X and R leads to a vibrational fine structure of the two components of the split "lone pair" PE.-band (see fig. 1). Some insight into this can also be gained from our model (6).

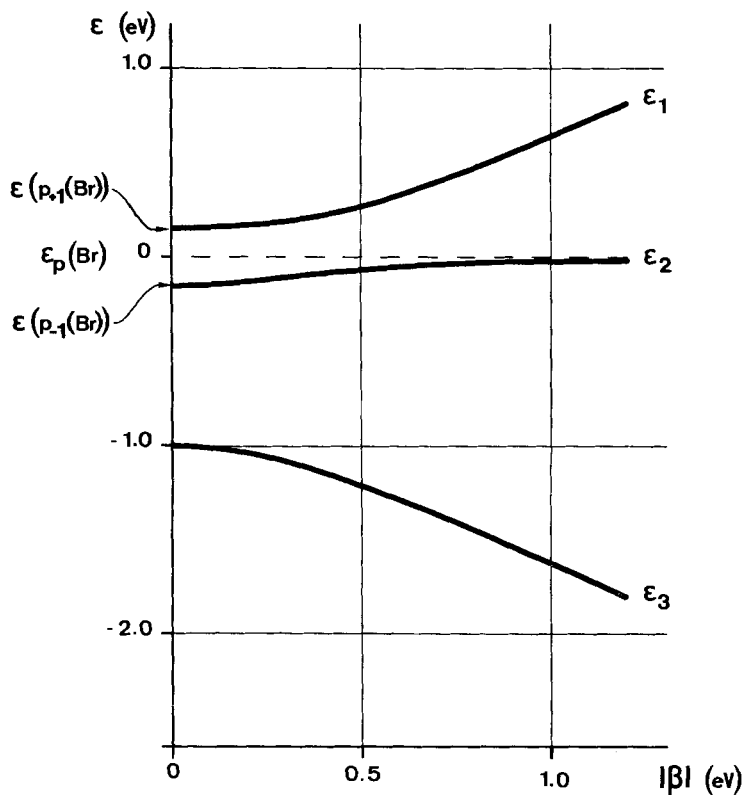
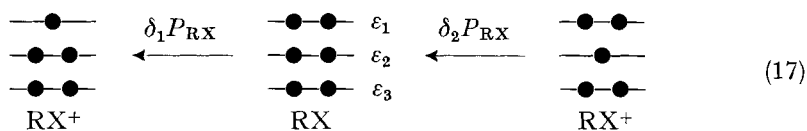


Fig. 2. Orbital energy correlation diagram for model (6) with  $X = \text{Br}$  ( $\zeta(\text{Br}) = 0.30 \text{ eV}$ ) and  $\varepsilon_p - \varepsilon_{p-1} = 1.0 \text{ eV}$

From the linear combinations  $\psi_1$ ,  $\psi_2$ ,  $\psi_3$  associated with the orbital energies  $\varepsilon_1$ ,  $\varepsilon_2$ ,  $\varepsilon_3$  we compute the generalized bond orders

$$P_{\text{RX}} = \sum_{j=1}^3 b_j c_{jX} c_{j\psi} \quad (16)$$

for the neutral molecule RX with numbers  $b_1 = b_2 = b_3 = 2$  and for the radical cation  $\text{RX}^+$  with  $b_1 = 1$ ,  $b_2 = b_3 = 2$  (ejection from  $\psi_1$ ) and  $b_2 = 1$ ,  $b_1 = b_3 = 2$  (ejection from  $\psi_2$ ).





The bond order changes,  $\delta_1 P_{\text{RX}}$  (ejection from  $\psi_1$ ) and  $\delta_2 P_{\text{RX}}$  (ejection from  $\psi_2$ ), which are listed in tab. 3 for the case  $X = \text{Br}$ , are postulated to be proportional to changes  $\delta r$  in as yet unspecified interatomic distances  $r$  on ionization:

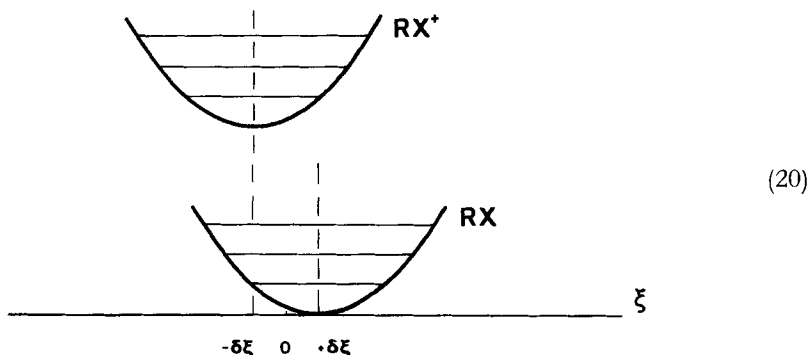
$$\delta r \propto -\delta_j P_{\text{RX}} \quad (18)$$

At first sight it might seem reasonable to identify  $r$  with the bond length  $r_{\text{CX}}$  of the carbon-halogen bond of the alkyl halide. However, at this stage we run into a slight difficulty which is due to the oversimplification of our model (6).

As can be seen from the first two examples given in fig. 1, the dominant spacing in the vibrational fine structure observed in the two components of the "lone pair" PE.-band is about  $1300 \text{ cm}^{-1}$  for compounds  $\text{RX}$  in which  $|\beta| < \zeta(\text{X})$ . This is much larger than expected for a vibration whose normal coordinate would involve mainly the stretching of the R-X bond ( $\tilde{\nu}(\text{R-Br}) \approx 560 \text{ cm}^{-1}$ ;  $\tilde{\nu}(\text{R-I}) \approx 500 \text{ cm}^{-1}$  [18]). Indeed, the observed spacing lies in a region characteristic for  $\text{CH}_2$  symmetric bending frequencies, *i. e.*  $\sim 1400 \text{ cm}^{-1}$  [18] [19]. This could be taken as an indication that the orbital  $\varphi(\text{R})$  which interacts with  $\text{np}_x(\text{X})$ , is essentially of the type  $(\sigma(\text{C-H}_{(a)}) - \sigma(\text{C-H}_{(b)}))/\sqrt{2}$  (*cf.* (6), *i. e.* a linear  $p_x$ -type combination of  $\text{CH-}\sigma$ -orbitals homoconjugating with  $\text{np}_x(\text{X})$  of the halogen atom. (This argument is supported by the observation that the "lone pair" bands in the PE.-spectra of secondary or tertiary alkylhalides exhibit a much narrower spaced, usually unresolved vibrational fine structure.) Therefore ejection of an electron from either  $\psi_1$  or  $\psi_2$  will lead also to a change in the HCH bond-angle. It is reasonable to assume that this change in bond-angle, and therefore the change  $\delta r_{\text{H}\dots\text{H}}$  in distance  $r_{\text{H}\dots\text{H}}$  between the two hydrogen atoms  $\text{H}_{(a)}$  and  $\text{H}_{(b)}$  (see (6)), is again proportional to  $\delta_j P_{\text{RX}}$ .

Let  $r$  now stand for the interatomic distance most severely affected by the ejection of an electron from either the orbital  $\psi_1$  or  $\psi_2$  (*e.g.*  $r_{\text{H}\dots\text{H}}$  or  $r_{\text{C-X}}$ ). As postulated in (18) the change  $\delta r$  is taken to be proportional to the bond order change  $\delta_j P_{\text{RX}}$ . We make the additional simplifying assumption that the normal vibration involving mainly the interatomic distance  $r$  and hence associated with the dominating progression in the PE.-band has the frequency  $\nu = c\tilde{\nu}$  both for the neutral molecule  $\text{RX}$  and for the radical cation  $\text{RX}^+$ . We express  $\delta r$  in units of  $a$  [20],

$$\delta r = 2 \cdot a \cdot \delta \xi \quad (19)$$



where  $a = (hc\tilde{\nu}/k)^{1/2}$  is the amplitude of a classical harmonic oscillator of frequency  $c \cdot \tilde{\nu}$  and force constant  $k$  whose energy equals the zero-point vibration energy  $E_0 = h\nu/2$  of its quantum-mechanical equivalent. (This means that for the particular harmonic oscillator the quantity  $a$  plays the role of a "Bohr-radius").

The *Franck-Condon* diagram (20) summarizes the situation for an ionization process  $RX \rightarrow RX^+ + e$  where the potential curve for the upper state ( $RX^+$ ) is shifted by  $2\delta\xi$  relative to the one for the lower state ( $RX$ ). (Diagram (20) implies that  $\delta r = 2a\delta\xi$  is negative. Note that our conclusions would be the same for  $\delta r$  positive).

It is easy to show [21] that the intensities  $W_{0\leftarrow 0}$  and  $W_{1\leftarrow 0}$  of the first two vibrational fine structure maxima of a progression in a PE.-band satisfy the relationship

$$W_{1\leftarrow 0}/W_{0\leftarrow 0} = 2(\delta\xi)^2 \quad (21)$$

if the coordinate  $\xi$  is associated in  $RX^+$  with a quadratic potential shifted by  $2\delta\xi$  relative to the one in  $RX$ , but having the same force constant  $k$ .

With the exception of cases such as cyclopropyl bromide (see fig. 1) we observe experimentally that the  $0 \leftarrow 0$ -transition is always the most intense one ( $W_{0\leftarrow 0} > W_{1\leftarrow 0}$ ). From (21) we deduce that this is true if  $\delta\xi < 1/\sqrt{2}$  or  $\delta r < a\sqrt{2}$ . In particular we find:

$W_{1\leftarrow 0}/W_{0\leftarrow 0}$	.0	.2	.4	.6	.8	1.0	
$\delta\xi$	.0	.32	.45	.45	.63	.71	(22)
$\delta r$	.0	.64a	.90a	1.10a	1.26a	1.42a	

This shows that observed intensity ratios  $W_{1\leftarrow 0}/W_{0\leftarrow 0}$ , which fall roughly into the interval 0.2 to 0.8, demand a change  $\delta r \sim a$  in the interatomic distance  $r$ .

If  $r \equiv r_{C-X}$ , then we have  $\tilde{\nu}(C-X) \approx 500 \text{ cm}^{-1}$  and  $k_{C-X} \approx 3 \cdot 10^5 \text{ dyn cm}^{-1}$  [18]. This yields  $a = 0.06 \text{ \AA}$ . On the other hand if  $r \equiv r_{H \dots H}$  then  $\tilde{\nu}(H \dots H) \approx 1400 \text{ cm}^{-1}$  (symmetric bending of the  $CH_2$ -group). Assuming a central force field which assigns a force constant  $k_{H \dots H}$  to the distance  $r_{H \dots H}$  one obtains  $k_{H \dots H} \approx 0.6 \cdot 10^5 \text{ dyn cm}^{-1}$ . From  $\tilde{\nu}(H \dots H)$  and  $k_{H \dots H}$  we calculate  $a = 0.02 \text{ \AA}$ . Both values ( $a = 0.06 \text{ \AA}$  for  $r_{C-X}$  and  $a = 0.02 \text{ \AA}$  for  $r_{H \dots H}$ ) are of reasonable magnitude for changes expected to accompany an adiabatic ionization process.

Table 3. Bond order changes  $\delta_J P_{RBr}$  for the ionization processes (17) of model (6) with  $X = Br$   
Differences  $\epsilon_p(Br) - \epsilon_\varphi(R)$  and resonance integrals  $\beta$  in eV

	$\beta = -.0$		$\beta = -.1$		$\beta = -.2$		$\beta = -.3$		$\beta = -.4$		$\beta = -.5$	
$\epsilon_p(Br) - \epsilon_\varphi(R)$	$\delta_1 P_{XR}$	$\delta_2 P_{XR}$	$\delta_1 P_{XR}$	$\delta_2 P_{XR}$	$\delta_1 P_{XR}$	$\delta_2 P_{XR}$	$\delta_1 P_{XR}$	$\delta_2 P_{XR}$	$\delta_1 P_{XR}$	$\delta_2 P_{XR}$	$\delta_1 P_{XR}$	$\delta_2 P_{XR}$
.5	.000	.000	.079	.121	.166	.159	.256	.135	.332	.095	.385	.065
1.0	.000	.000	.045	.055	.094	.095	.150	.110	.212	.100	.270	.085
1.5	.000	.000	.031	.036	.065	.065	.103	.084	.147	.090	.195	.085
2.0	.000	.000	.024	.027	.049	.049	.078	.067	.111	.076	.148	.077
2.5	.000	.000	.019	.021	.039	.040	.062	.055	.088	.065	.117	.069

From tab. 3 and fig. 3 (which again refers to the particular case  $RBr$  with  $\epsilon_p - \epsilon_\varphi = 1.0 \text{ eV}$ ) we see that ejection of an electron from the orbital  $\psi_1$  will lead, according

to (18), to an increase in  $\delta r$  with increasing values of  $|\beta|$ . In contrast, ejection from  $\psi_2$  will yield approximately the same  $\delta r$  if  $|\beta| < \sim 0.3$  eV, but for larger  $|\beta|$  the bond order changes  $\delta_2 P_{RX}$ , and thus  $\delta r$  will drop again to become zero as  $|\beta|$  tends to infinity. From this behaviour of  $\delta_1 P_{RX}$  and  $\delta_2 P_{RX}$  we predict that for moderately

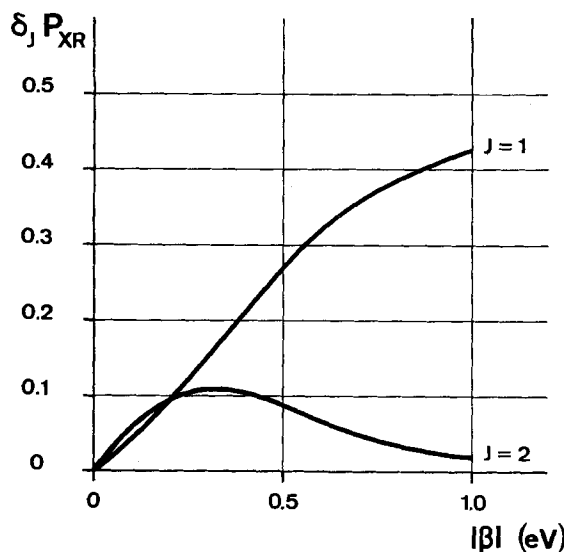


Fig. 3. Dependence of the bond order changes  $\delta_1 P_{RX}$  and  $\delta_2 P_{RX}$  on  $\beta$  for model (6) with  $X = Br(\zeta(Br) = 0.30$  eV) and  $\epsilon_p - \epsilon_\varphi = 1.0$  eV (See also fig. 2)

conjugating alkyl groups both components of the split "lone pair" band will exhibit roughly the same vibrational fine structure patterns. However, for larger conjugative interaction (e.g. R = cyclopropyl) the component at lower ionization potential, correlated with ejection from  $\psi_1$ , will broaden to a band with maximum intensity at higher vibrational excitation. In contrast, the second component should sharpen up again to a band dominated by the  $0 \leftarrow 0$  transition. This is exactly what is observed.

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## 147. Organic Phosphorus Compounds 52<sup>1)</sup>

### Preparation and Properties of $\beta$ -Hydroxyalkyl-phosphonium Salts and Tertiary Phosphine Oxides

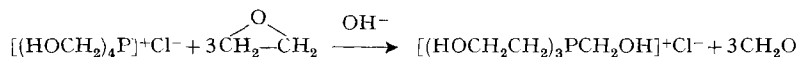
by **Ludwig Maier**

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(27. V. 71)

*Summary.* The new, tris-(2-hydroxyalkyl)-(hydroxymethyl)-phosphonium salts: [(RCHOHCH<sub>2</sub>)<sub>3</sub>PCH<sub>2</sub>OH]Cl (I, R = ClCH<sub>2</sub>; III, R = CH<sub>3</sub>) are formed in high yield by reaction of tetrakis-(hydroxymethyl)-phosphonium chloride (Tetrakis) with epoxides under basic conditions. Under the same conditions, styrene oxide yields only the disubstituted product, [(PhCHOHCH<sub>2</sub>)<sub>2</sub>(CH<sub>2</sub>OH)<sub>2</sub>P]Cl. Optimal pH values for the reactions are 8 to 9; at lower pH the conversion is too slow; at a higher pH, oxidative decomposition of the salts occurs. Conversion of the salts to tertiary phosphine oxides (RCHOHCH<sub>2</sub>)<sub>3</sub>P=O (R = ClCH<sub>2</sub>; CH<sub>3</sub>) with loss of the hydroxymethyl group is best carried out with chlorine at pH 5 to 7. The yields are usually 60 to 90%.

The synthesis of tris-( $\beta$ -hydroxyethyl)-hydroxymethyl-phosphonium chloride [2] by reaction of tetrakis-(hydroxymethyl)-phosphonium chloride (Tetrakis) with ethylene oxide under basic conditions [2b] has been described.



It seemed of interest to explore the scope of this reaction, all the more as only a few examples are known where Tetrakis has undergone reaction resulting in the formation of new carbon-phosphorus bonds [3]. Thus base treatment of Tetrakis

<sup>1)</sup> For n° 51 of this series, see [1].