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Preliminary communication

Theory and application of photoelectron spectroscopy XXX*. Hg–C hyperconjugation

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SUMMARY

Evidence for a hyperconjugative splitting due to the interacting Hg–C σ_u and ethylene $\pi(b_{1u})$ MOs in allylmercuric chloride is presented.

Consider a π MO (energy = E_π) and a σ MO (energy = E_σ, with $E_\sigma < E_\pi$). Provided the two MOs overlap the π MO will be destabilized by $|\delta E|$ and the σ MO stabilized by $|\delta E|$. $|\delta E|$ is given as[1]:

$$|\delta E| = \frac{(H_{\sigma\pi})^2}{\Delta E} \qquad (1)$$

where $\Delta E = |E_\pi - E_\sigma|$. and $H_{\sigma\pi}$ is a measure of the interaction between the σ and π MOs.

Using the photoelectron (PE) spectrum of allylmercuric chloride, $CH_2{=}CH{-}CH_2HgCl$ (I) we present below a unique example for the applicability of (1), and derive the first quantitative description of Hg–C hyperconjugation[2].

Figure 1 shows the PE spectrum of (I). The bands in this spectrum can be easily assigned by comparison with the PE spectrum[3] of methylmercuric chloride, MeHgCl (II). (1) must be attributed to ionization from the π MO, (2) and (3) to ionization from the lone pair MOs on the Cl atom, (4) and (5) to ionization from the σ_u(C–Hg) and σ_g(C–Hg) MOs**, (6) and (7) to ionization from several σ(C–C) and σ(C–H) MOs and finally (8) is the first

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[*] For part XXIX see ref. 13.
[**] The σ_g(C–Hg) ionization in (I) is superimposed on the σ(C–C) and σ(C–H) ionization range.

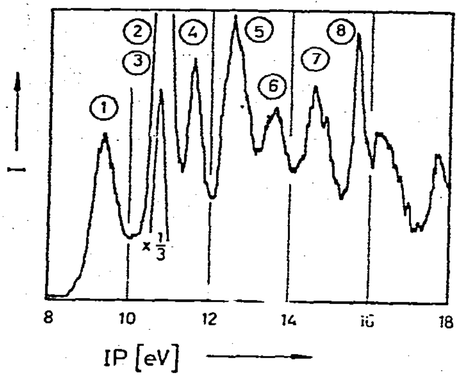
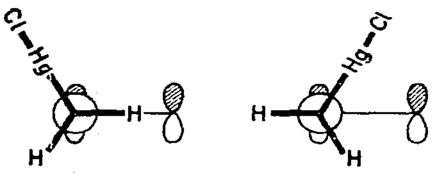


Fig. 1. Photoelectron spectrum of allylmercuric chloride (I). The vertical ionization potentials (in eV) are: (1) 9.35, (2) and (3) 10.75, (4) 11.55, (5) 12.50, (6) 13.6, (7) 14.6 and (8) 15.61.

member of a group of bands due to ionization from the $5d^{10}$ shell of the mercury atom.



(I) exists only in one *gauche* formation[4]. In this, there may be, in addition to an inductive effect of the HgCl substituent on the π MO, hyperconjugative interaction between, on the one hand, a C–H MO and the π MO and, on the other, a C–Hg MO and the π MO. The inductive effect of HgCl is 0.0 eV[5]. The hyperconjugative destabilization of the π MO due to its overlap with the C–H MO in a *gauche* position is 0.31 eV[6]. Consequently, C–H hyperconjugation excluding the π MO would lie at 9.66 eV. Hence the destabilization of the π MO due to its overlap with the Hg–C MO, compared with the energy of this MO in ethylene ($\pi(b_{1u})$ MO = 10.51 eV[7]), amounts to 0.85 eV. Provided (1) can be applied then the σ_u(Hg–C) MO in (I) must be more stable than the σ_u(Hg–C) MO (10.8 eV[3]) in (II) by almost the same amount. This condition is very well satisfied as the splitting pattern shows, and thus from (1) we obtain for the σ(Hg–C)/π (ethylene) interaction $H_{\sigma\pi}$ = 0.5 eV (Fig.2).

This wholly novel observation, namely a clear experimental demonstration of a hyperconjugative splitting, was not possible in the case of the PE spectra of other allyl compounds, $CH_2{=}CH{-}CH_2X$ (X = Me[6], CMe_3[6], $SiMe_3$[6,8,9], $GeEt_3$[9], $SnBu_3$[9], F[10], Cl[10], Br[10], I[10] and SMe[11,12]), because in these systems the bands of the σ MOs involved in the hyperconjugative interaction overlap strongly with other bands.

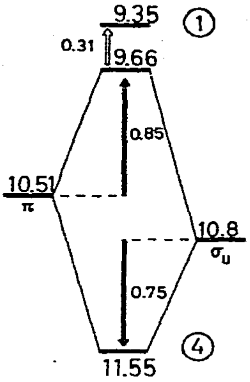


Fig. 2.

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