Inorganica Chimica Acta, 37 (1979) L517–L519
©Elsevier Sequoia S.A., Lausanne – Printed in Switzerland

UV Spectrum and WH–EH–MO Description of Methylcobalt Tetracarbonyl

FERENC CSER[a], VILMOS GALAMB and GYULA PÁLYI*

Research Group for Petrochemistry of the Hungarian Academy of Sciences, H-8200 Veszprém, Hungary

Received June 20, 1979

Methylcobalt tetracarbonyl, $CH_3Co(CO)_4$, (*I*) has been known for more than two decades but in spite of its importance as the simplest alkylcobalt carbonyl, not much has been reported about its chemical and physical behaviour. This is obviously caused by its instability and tendency to transform to acetylcobalt tetracarbonyl $CH_3COCo(CO)_4$, (*II*). Even the observation of its IR spectrum met considerable experimental difficulties [2].

We were interested in the quantum chemical analysis of certain alkylcobalt carbonyls [3] but we first needed the interpretation of (*I*) as reference compound. The only MO study [4] concerning (*I*) reported incomplete data (rotational barrier and energy of the trigonal bipyramidal and tetragonal pyramidal configurations). We performed a complete Wolfsberg–Helmholtz (Extended Hückel) MO [5] analysis of (*I*) the parameters of which were fitted to the UV absorption bands.

The UV spectrum was obtained in vapour phase utilizing the fact that (*I*) is volatile under atmospheric conditions while the contaminating (*II*) is not. We prepared Et_2O solutions of (*I*) from $Na[Co(CO)_4]$ and CH_3I according to Hieber *et al.* [2]. A few drops of this solution were placed in a 100 mm long UV gas cell sealed with Ar gas and then the spectrum was quickly registered. The observed spectra were compared with those of CH_3I and (*II*) to avoid misinterpretation. Bands of the observed spectra were resolved by deconvolution. Two bands could be observed at $\lambda_1 = 215$ nm (5.76 eV) (100) and $\lambda_2 = 245$ nm (5.06 eV) (~ 1, sh). Absorbance could not be determined since the concentration of (*I*) was not known.

Our WH–EH–MO calculations were based on the structural parameters shown in Table I.

Trigonal bipyramidal array with the methyl group in axial position has been accepted following the IR spectroscopic results of Bor [7] and the calculations of Demuynck *et al.* [4].

Diagonal elements of the Hamiltonian were taken as $H_{ii} = U_i$ (eV), off-diagonal elements as $H_{ij} = 0.5\,KS_{ij}(U_i + U_j)$ ($K = 1.75$ according to ref. 5b). S_{ij} values were calculated using Slater orbital exponents (ζ_i). Values of U_i and ζ_i are shown in Table I. U_is for Co were taken initially from refs. 8–11 but partial charges and excitation energies obtained using these data were irreal. Then we tested the parameters (U_i and ζ) from ref. 12 and we obtained a high negative charge (−1.95) on the Co but the first excitation energy was still 2.6 eV, much below the observed. Finally we chose the U_i values shown in Table I as a compromise for Co. The rest (C, O and H) of the U_i values were taken from ref. 13, Slater orbital exponents from ref. 14.

---

[a] Research Institute for Plastics, Budapest, Hungary.

*Author to whom correspondence should be addressed.

TABLE I. Starting Data for Calculations.[a]

Geometry

Bond	Bond Length, pm	Ref.
Co, C_{Me}	206	4
C_{Me}, H	108	4, 6
Co, C_{ax}	174	4, 6
Co, C_{equ}	180	4, 6
C, O	116	4

MO Parameters

Data	s			p			d			
Atom	n_i	U_i	ζ_i	n_i	U_i	ζ_i	n_i	U_i	ζ_i	N_j
Co	4	15.657	1.054	4	11.659	1.054	3	27.836	2.30	9
C	2	21.40	1.625	2	11.40	1.625	–	–	–	4
O	2	28.48	2.275	2	13.80	2.275	–	–	–	6
H	1	13.60	1.00	–	–	–	–	–	–	1

[a] Notation: H_i, Hamiltonian of the ith orbital; U_i, ionization potential of the ith atomic orbital; n_i, principal quantum number; ζ_i, Slater exponent of the ith atomic orbital; N_j, sum of the valence electrons on atom j.

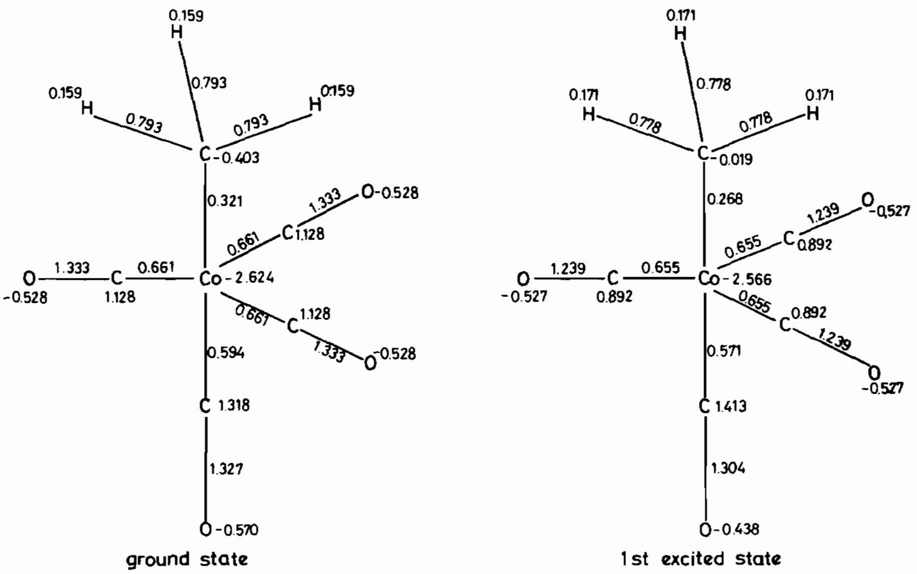

Fig. 1. Partial charges and overlap populations of methylcobalt tetracarbonyl in the ground and first excited state.

TABLE II. The Characteristics of the Highest Energy Occupied and the Lowest Energy Unoccupied Molecular Orbitals.

Ground State		
Orbital[a]	Energy, eV	Weight of Components (%)
ψ_{25}	14.42	15.3 CO_{ax}; 84.7 CO_{equ}
ψ_{26}	13.21	10.3 Co; 72.6 Me; 3.7 CO_{ax}; 13.4 CO_{equ}
ψ_{27}	13.21	1.7 Co; 30.3 Me; 2.4 CO_{ax}; 65.6 CO_{equ}
ψ_{28}	13.17	3.6 Co; 50.4 Me; 1.3 CO_{ax}; 44.7 CO_{equ}
1st Excited State		
ψ_{30}	9.01	0.1 Co; 9.4 Me; 5.7 CO_{ax}; 84.8 CO_{equ}
ψ_{29}	8.52	33.2 Co; 52.0 Me; 3.8 CO_{ax}; 11.0 CO_{equ}
ψ_{31}	8.52	0.7 Co; 14.0 Me; 9.8 CO_{ax}; 75.5 CO_{equ}
ψ_{32}	8.50	1.7 Co; 35.7 Me; 20.5 CO_{ax}; 42.1 CO_{equ}

[a] The numbering of the orbitals follows the order of energy.

The computation was carried out with a Fortran program [15] based on the Algol program of Mezey [16] and performed using a CDC 3300 computer.

Charges were calculated using a Mulliken overlap population analysis [17]. Energy barriers to internal rotation of the methyl group were taken as the difference of total energies corresponding to various rotational angles.

Rotation of the methyl group around the Co, C_{Me} axis yields a threefold barrier of 0.16 eV height which agrees well with the results of an *ab initio* calculation [4] (0.08 eV).

Partial charges and overlap populations in the ground and first excited states of the lowest energy configuration are shown in Fig. 1. However, the absolute values of the charges should be taken with care, these are overestimated following the neglect of the repulsion and exchange integrals [13].

None of the filled or empty orbitals was separated energetically well enough from the rest of both kinds to be identified as HOMO or LUMO respectively. There are two sets of highest occupied and unoccupied orbitals which could be regarded as FMOs (Table II). These orbitals are separated by ~ 1.2 eV from the rest. The highest energy occupied and unoccupied orbitals are separated by ~ 4.1–5.6 eV from each other, this agrees well with the observed E_2 = 5.06 eV corresponding to the lower energy UV band.

The MOs which can be regarded as FMOs are associated with more groups and not quite clearly localized as shown in Table II. This situation is not unprecedented in such type of calculations [18].

However, both these data and the distribution of charges predict the methyl group as the site of electrophilic and the equatorial CO groups as the site of nucleophilic attack. This result provides a further independent support to the presently accepted mechanism [19, 20] of the 'CO insertion' reaction of alkylcobalt carbonyls, which is one of the key steps in the hydroformylation of olefins.

The Mulliken populations are in good agreement with the interpretation of σ- and π-electronic effects in similar compounds which was based on NMR data [21].

The qualitative and quantitative agreement of certain results of this work with those of other independent studies [4, 21] can be regarded as evidence for the reliability of our results which seem thus to be applicable to further similar calculations.

Acknowledgements

The authors are grateful to Profs. L. Markó (Veszprém) and G. Hardy (Budapest) for supporting this work, to Prof. P. Mezey (Saskatoon) for making his computer program available as well as to him and Dr. Á. Kiss (Budapest) for valuable discussions.

References

1 W. Hieber, O. Vohler and G. Braun, *Z. Naturforsch., 13b,* 192 (1958).
2 L. Markó, G. Bor, G. Almásy and P. Szabó, *Brennstoff-Chem., 44,* 184 (1963).
3 G. Pályi, *Transition Met. Chem., 2,* 273 (1977).
4 J. Demuynck, A. Strich and A. Veillard, *Nouv. J. Chim., 1,* 217 (1977).
5 (a) M. Wolfsberg and L. Helmholtz, *J. Chem. Phys., 20,* 837 (1952); (b) R. Hoffmann, *J. Chem. Phys., 39,* 1397 (1963).
6 J. P. Grima, F. Choplin and G. Kaufmann, *J. Organometal. Chem., 129,* 221 (1977).
7 G. Bor, *Inorg. Chim. Acta, 1,* 81 (1967).
8 D. W. Clack, N. S. Hush and J. R. Yandle, *J. Chem. Phys., 57,* 3503 (1972).
9 A. B. Anderson, *Inorg. Chem., 15,* 2598 (1976).
10 J. Hinze and H. H. Jaffé, *Can. J. Chem., 41,* 1315 (1963).
11 J. H. Schachtschneider, R. Prius and P. Ros, *Inorg. Chim. Acta, 1,* 462 (1967).
12 R. H. Summerville and R. Hoffmann, *J. Am. Chem. Soc., 98,* 7240 (1976).
13 A. Botrel and C. R. Guérilot, *J. Chim. Phys., 71,* 979 (1974).
14 J. C. Slater, *Phys. Rev., 36,* 57 (1930).
15 F. Cser, unpublished, available upon request.
16 P. Mezey, unpublished.
17 R. S. Mulliken, *J. Chem. Phys., 23,* 1833, 1841, 2338, 2343 (1955).
18 T. F. Block, R. F. Fenske and C. P. Casey, *J. Am. Chem. Soc., 98,* 441 (1976).
19 Z. Nagy-Magos, G. Bor and L. Markó, *J. Organometal. Chem., 14,* 205 (1968).
20 F. Calderazzo, *Angew. Chem., 89,* 305 (1977).
21 J. D. Duncan, J. C. Green, M. L. H. Green and K. A. McLauchlan, *Chem. Commun.,* 721 (1968).