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THEORETICAL INVESTIGATION ON HYDROFORMYLATION REACTIONS

I. STRUCTURES AND REACTIVITIES OF COBALT CARBONYLS AND HYDROCARBONYLS

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Summary

Extended Hückel Theory calculations have been carried out in a study of the most important cobalt carbonyls and hydrocarbonyls involved in the hydroformylation reaction. The geometries of the stable isomers of $Co_2(CO)_8$, $Co_2(CO)_7$, $Co(CO)_4$, $Co(CO)_3$ have been calculated and used to interpret the changes in the IR spectrum of $Co_2(CO)_8$ observed on varying the temperature. The reaction paths for the interconversions of the stable isomers have also been investigated. The optimized geometry of $HCo(CO)_4$ agrees well with the experimental structure. The C_s symmetry found for the most stable isomer of $HCo(CO)_3$ is of much interest, serves to explain the formation of the complex with olefins.

Introduction

The study of the mechanism of the hydroformylation reaction (oxo-synthesis) of olefins (eq. 1) has always aroused considerable interest. In spite of the

$$RCH{=}CHR' + CO + H_2 \overset{cat}{\rightarrow} RCH(CHO)CH_2R' + RCH_2(CHO)R' \qquad (1)$$

large amount of work done in this field, many aspects of the mechanism are still uncertain. An improved knowledge of the details of this reaction is important since oxo-synthesis is a widely used industrial process [1,2], and, in this respect understanding of the selectivity (regio and stereo) and the determination of the species which are catalytically active under different conditions are problems of prime interest. The reaction is catalysed by several complexes of transition metals (Fe, Co, Pd, Rh, Pt are the most used) and among them cobalt and rhodium carbonyls have been successfully employed and extensively investigated [3].

The question of the geometries of the catalytic species suggested by experimentalists has been considered in previous theoretical studies [4,5], but the complexity of the systems required either the restriction of the study to the best known geometries or limitation of the number of the variables in the energy minimization processes. Even more difficult is the choice of the number and type of the key steps in the reaction.

In the present paper we focus our attention on the cobalt carbonyls and hydrocarbonyls as, from a theoretical viewpoint, they are the simplest catalytic complexes used in the process. In fact, $Co_2(CO)_8$ and $HCo(CO)_4$ are catalyst precursors for the reaction, while $Co_2(CO)_7$, $HCo(CO)_3$ and other species have been proposed as catalytic intermediates [1,6]. This means that all the complexes derived from the reaction between $Co_2(CO)_8$ and H_2 [7] might participate in the hydroformylation process.

Some of the complexes mentioned have been investigated independently of the oxo process by IR and Raman spectroscopy [8—14], electron and X-ray diffraction [15,16], and ESR spectroscopy [13,17]. In the calculations, in order to permit energy minimization with respect to the largest number of variables, a fast semiempirical method was used. The Extended Hückel Theory (EHT) [18] was used because it gave reasonably good predictions in the earlier studies of structural problems of transition metal compounds [19—22] without requiring excessive computer time. If the EHT method is properly used, some objections to it (e.g. see ref. 23) are avoided [24,25].

Method of calculation

EHT was used in the standard formulation, implying the solution of the matrix equation $(H - ES)C = O$ where S is the overlap matrix of Slater type (single ζ) atomic orbitals. In this method, the diagonal matrix elements H_{ii} correspond to the valence state ionization potentials, and the adopted values are listed in Table 1, together with Slater exponents and the bond lengths, which were kept fixed throughout the calculations. Off diagonal elements H_{ij} were obtained by the Wolfsberg—Helmholz equation [26] using the same parameters. It should be noted that various values for $H_{3d\,3d}$(Co) are reported

TABLE 1

PARAMETERS USED IN EHT CALCULATIONS [a]

	Slater exponents	H_{ii} (eV)	Bond lengths (Å) [b]	
C	1.62 (2s, 2p)	—23.0 (2s), —13.4 (2p)	Co—C	1.80
O	2.28 (2s, 2p)	—33.9 (2s), —16.4 (2p)	C—O	1.17
H	1.30 (1s)	—13.6 (1s)	Co—H	1.60
Co	2.00 (3d)	—17.9 (3d)		
	1.60 (4s, 4p)	—8.0 (4s), —8.0 (4p)		
		$K = 1.80$		

[a] Ref. 27. [b] Mean values from data quoted in ref. 15,16.

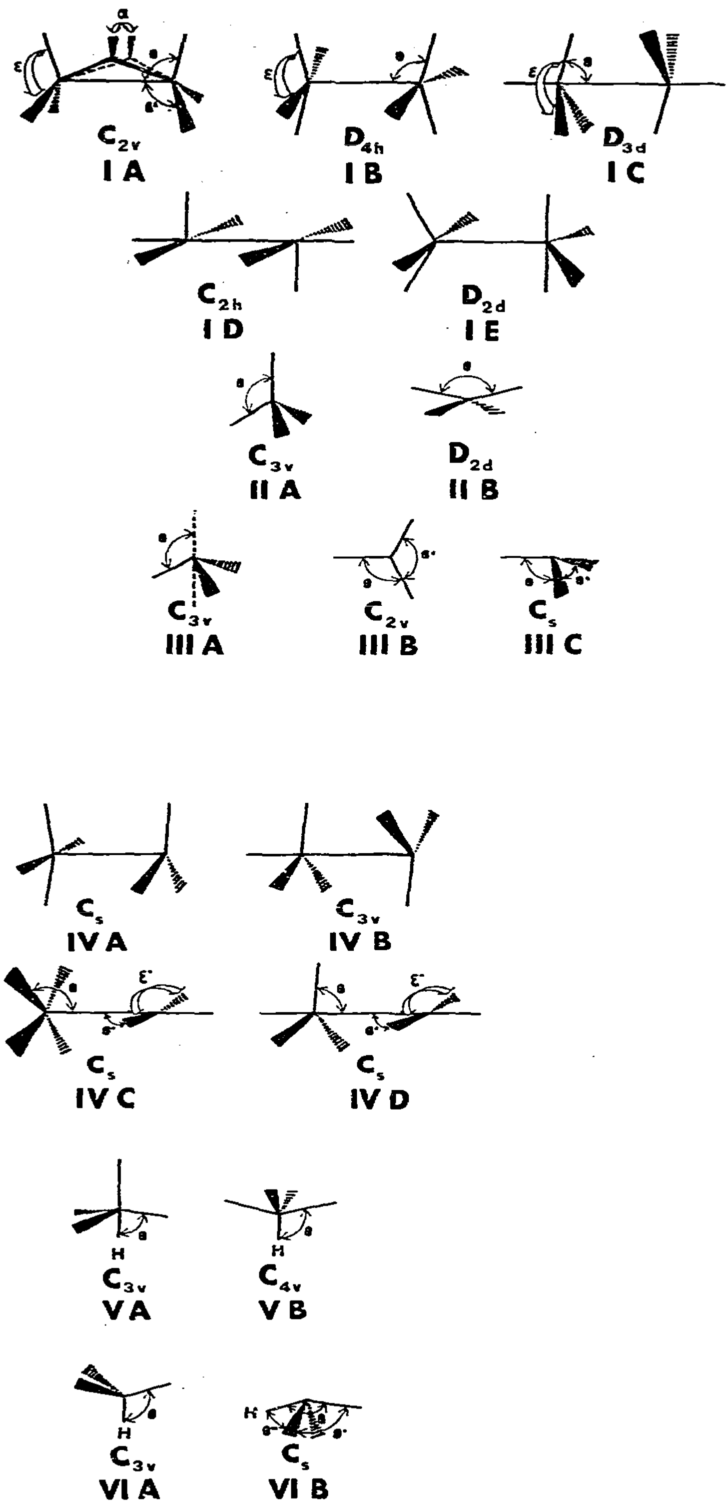

Fig. 1. Geometries and symmetries of the structures considered.

in the literature. In order to check the sensitivity of the results to the parameters mentioned, the geometries of hydrocarbonyls were also optimized using $H_{3d\,3d} = -12$ eV. The results were coincident in the case of $HCo(CO)_4$, and were not significantly changed for $HCo(CO)_3$. Well conscious of the inability of EHT to reproduce bond lengths when first row atoms are involved, we fixed C—O, Co—H and Co—C distances at their average experimental values (see Table 1). The Co—Co distances, on the other hand were always optimized. We were able to minimize the total energy as a function of all the angular parameters, and to ascertain whether or not the removal of symmetry constraints might lead to lower energies in the systems considered. Powell's technique [28], based on conjugated directions, was employed for automatic optimization of the geometrical parameters.

Results and discussion

$Co_2(CO)_8$. This compound exists in the solid state as a bridged structure [15], here referred to as IA in Fig. 1, which has been completely resolved by X-ray diffraction. There is spectroscopic evidence that both in solution [8—11] and in a matrix [12] at least two non-bridged isomers are present. However, the isomers were not isolated nor unequivocally identified.

The main purpose of our work was to determine the geometries of the stable isomers of $Co_2(CO)_8$, and to investigate the mechanisms of their interconversions. Of the various structures used in interpreting the spectroscopic data [8,12], those specified in Fig. 1 and referred to as IA—IE were taken into consideration. EHT calculations proved that the structures ID and IE do not refer to stable isomers, unlike structures IA, IB, IC. Optimized geometries, together with the corresponding total energies are shown in Table 2. It is clear from the

TABLE 2

EHT ENERGIES, GEOMETRIES AND SYMMETRIES OF ISOMERS IA, IB, IC OF $Co_2(CO)_8$ AND IVC, IVD OF $Co_2(CO)_7$

	$Co_2(CO)_8$				$Co_2(CO)_7$	
	Bridged structure		Non bridged structures			
	IA Exp. [a]	IA Calc.	IB Calc.	IC Calc.	IVC Calc.	IVD Calc.
Symmetry	C_s	C_{2v}	D_{4h}	D_{3d}	C_s	C_s
Co—Co (Å)	2.52	2.56	2.87	2.88	2.73	2.79
θ [b]	116	119	97	84	97	82
θ' [b]	109 124	116			84	89
ϵ [b]	113 122	127	90	120	90	120
ϵ' [b]					170	169
α [b]	127	130				
E (eV)		—2089.85	—2088.90	—2088.66	—1868.73	—1868.69

[a] Ref. 15. [b] See Fig. 1.

listed data that the geometry of structure IA optimized by EHT calculations agrees very well with the experimental one. In regard to non-bridged stable isomers, IC appears staggered, while in the case of IB a nearly free rotation about the Co—Co bond is found, with a slight preference for the eclipsed D_{4h} symmetry. As for the relative energies, isomer IA is the most stable, followed by IB and IC. The serious limitations of EHT in predicting the absolute values of the total energy are well known. However, we feel that the trend of total energy vs. φ, shown in Fig. 2, gives a correct qualitative interpretation of the stabilities of the three isomers and of their interconversion processes, even if the energy barriers are probably overestimated. Our confidence arises from the care we took in the minimization process for each value of the reaction coordinate to allow the structures to be free from symmetry constraints. The symmetries reported in Table 2 were thus themselves determined by the calculations. The reaction path in Fig. 2 shows clearly the two isomerization barriers governing the passage from IA to IB and from IB to IC; the barrier heights have to be related to the following values of ΔH^0 obtained by Bor et al. [10]: $\Delta H^0_{1\to2} = 1.25$ kcal/mol and $\Delta H^0_{2\to3} = 0.96$ kcal/mol from IR spectra (1, 2, 3 refer to isomers of highest, intermediate, and lowest stability respectively).

The calculated Co—Co bond lengths for the three isomers and bond strengths for the non-bridged ones are: IA: 2.56 Å; IB: 2.87 Å, 48.5 kcal/mol; IC: 2.88 Å, 41.9 kcal/mol, respectively. It appears that Co—Co bond lengthens from IA to IC. On the basis of the analysis of the intensities of the Raman Co—Co stretchings by Onaka and Shriver [11] it can be deduced that the Co—Co stretching frequency of isomer 2 is higher than that of 3, with a ratio of the corresponding force constants of about 0.75; this accords well with the value 0.86 predicted by the EHT calculations.

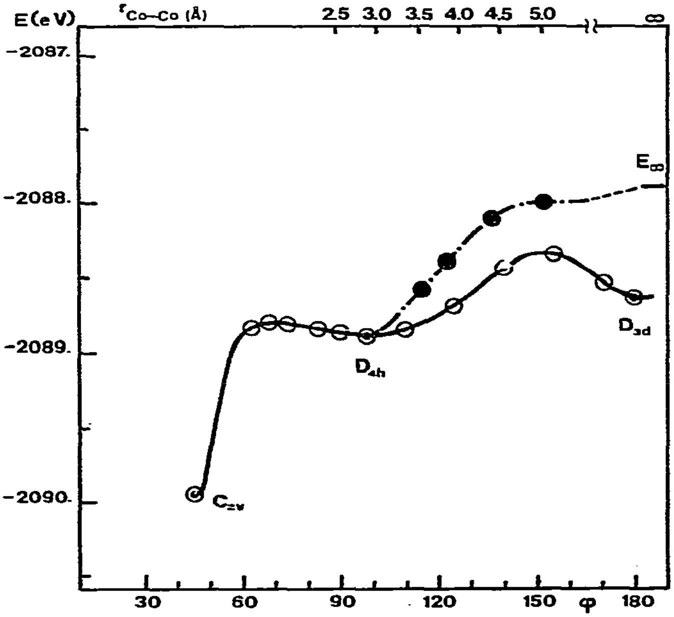

Fig. 2. Pathways of the interconversion processes for the stable isomers of $Co_2(CO)_8$ (○), and of decomposition reaction $Co_2(CO)_8 \rightleftharpoons 2\,\dot{C}o(CO)_4$ (●). φ is the angle between Co—Co and Co—C_{bridge} bonds.

The energy diagram of the highest occupied (ten), and lowest unoccupied (six) MO's for the three isomers are shown in Fig. 3, where the point group symmetry for each orbital is also shown. The highest occupied MO's (HOMO's) involve participation from both carbonyl and Co orbitals with large delocalization, and no correlation can be found among the HOMO's of the three isomers. In contrast the lowest unoccupied MO's (LUMO's) appear well characterized, as Co orbitals are absent and considerable contributions from p orbitals of carbonyls are found, with the carbon p_z orbitals predominating.

The results can be used to explaining the symmetry assignments made by the experimentalists in order to interpret the spectroscopic data for $Co_2(CO)_8$. Bor et al. [8—10] on the basis of IR spectra recorded in solution at different temperatures assign two stretching frequencies to the isomer of intermediate stability 2 and three to the isomer of lowest stability 3. Our results support these assignments, by the two and three distinct IR C—O stretching frequencies being compatible with the symmetries of structures IB, D_{4h}, and IC, D_{3d}, respectively. It

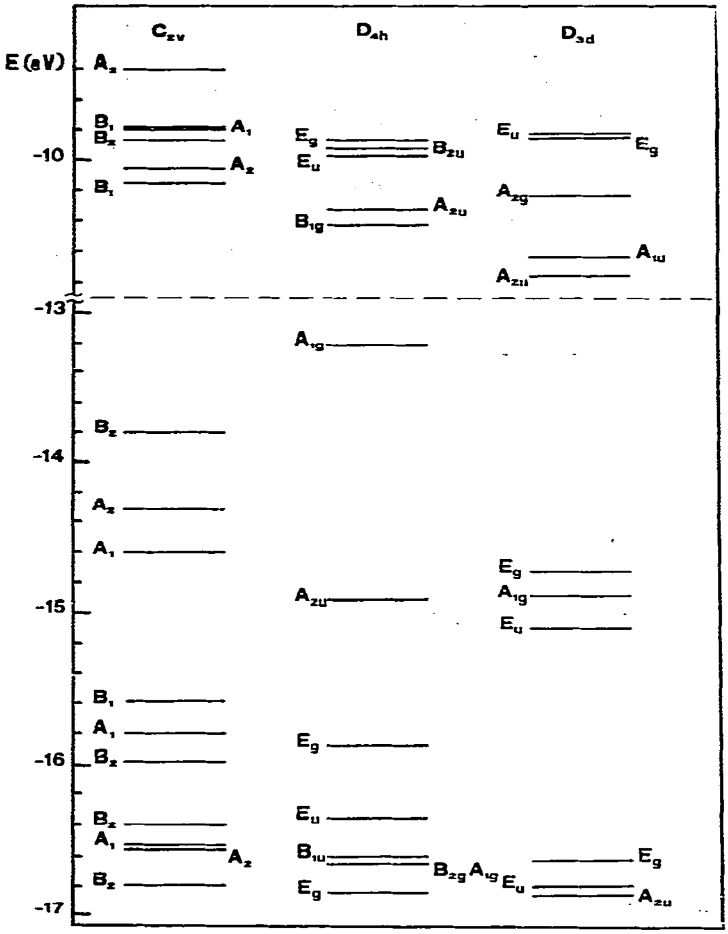

Fig. 3. Energy diagram and symmetries of the highest occupied (ten) and the lowest unoccupied (six) molecular orbitals for the three isomers of $Co_2(CO)_8$.

must be pointed out, however, that the assignment of the structure to the isomer of intermediate stability was proposed by Noack on the basis of a comparison with related compounds such as $CdCo_2(CO)_8$ and $HgCo_2(CO)_8$ [8]. On the basis of the IR spectra of $Co_2(CO)_8$ in Ar, hexane and other matrices, Sweany and Brown [12] assign three C—O stretching frequencies to isomer 2, and predict structure IC for it, while four bands are attributed to isomer 3, for which structures ID and IE are proposed. From our calculations, however, ID and IE appear to be unstable. The extra stretching frequency given in ref. 12 might possibly be due to perturbations of the spectrum by the matrix.

Photolysis experiments on $Co_2(CO)_8$ suggest that the interconversion $Co_2(CO)_8 \rightleftharpoons 2\ Co(CO)_4$ takes place so readily as to make its detection impossible [14]. $Co(CO)_4$ was also suggested to participate in the equilibrium of the $Co_2(CO)_8$ isomers in solution at high temperature [9,10], and it has been found that $Co(CO)_4$ is reversibly formed above 150°C, with $\Delta H^0 = 24 \pm 3$ kcal/mol. This value accords very well with the corresponding values found by thermochemical experiments for Co—Co bond, that is 20.6 or 22 kcal/mol [29,30].

It is plausible that the breaking of the Co—Co bond takes place more easily when starting from a non-bridged isomer, and so our study of the dissociation of $Co_2(CO)_8$ was carried out with isomer IB. It emerges from the calculations that as the Co—Co bond length increases the fragments quickly assume the structure of free radicals. During the process the energy increases monotonically as shown in Fig. 2. The lack of a barrier can explain the high efficiency of the interconversion between $Co_2(CO)_8$ and the unstable biradical. The calculated dissociation energies for IB and IC isomers of $Co_2(CO)_8$ are 23 and 18 kcal/mol, respectively.

Spectroscopic investigations on $Co(CO)_4$ have been carried out on samples isolated in a solid matrix [13], and on obtained sublimation of $Co_2(CO)_8$ [17]. IR, Raman and ESR spectra in vacuo [17] and in various matrices [13] suggest the existence of two isomers of the radical, with the symmetries C_{3v} IIA and D_{2d} IIB, respectively. The latter was also proposed by Hoffmann [20] and by Burdett [31] on the basis of theoretical considerations.

Our EHT calculations indicate that there is only one stable isomer, with D_{2d} symmetry, even though the energy difference from that of the planar structure is very small, while the C_{3v} symmetry structure is unstable. However, owing to the flatness of the energy surface and the approximate nature of the method the ϑ angle cannot be reliably specified.

The spectroscopic techniques used for the detection of $Co(CO)_4$ were also employed for the study of the radical $Co(CO)_3$ [13], and a slightly distorted D_{3h} geometry was indicated. Theoretical investigations performed by Hoffmann [20] and Burdett [31] suggest structures of C_{3v} IIIA and C_{2v} IIIB symmetries, respectively, while our EHT calculations predict the existence of only one stable isomer, the almost planar IIIC of C_s symmetry. The geometric parameters for $Co(CO)_4$ and $Co(CO)_3$ are listed in Table 3.

$Co_2(CO)_7$. This compound has been proposed as an intermediate species in the reactions [7,32,33]:

$$Co_2(CO)_8 + H_2 \rightleftharpoons 2\ HCo(CO)_4$$

$$2\ Co_2(CO)_8 \rightleftharpoons Co_4(CO)_{12} + 4\ CO$$

It was detected among the products of photolysis [14]:

$Co_2(CO)_8 \rightleftharpoons Co_2(CO)_7 + CO$

As for the possible geometries of $Co_2(CO)_7$, the IR spectrum in solid matrix [14] shows no absorptions characteristic of bridging carbonyl groups; moreover, the $Co_2(CO)_8$ resulting from the recombination after photolysis is predominantly the isomer 3.

In the light of this we studied only the possible non-bridged structures; this choice is supported by the fact that non-bridged isomers of $Co_2(CO)_8$ predominate at the pressures and temperatures at which hydroformylation is carried out.

The more obvious result of the removal of a carbonyl from structures IB and IC would be geometries IVA and IVB of Fig, 1, but these proved to belong to unstable species. If left free from symmetry constraints, they deform, without any energy barrier, into the stable isomers IVC and IVD, both of C_s symmetry.

The geometrical parameters for structures IVC and IVD are shown in Table 2. Fig. 4 shows the path for isomerization from IVC to IVD, where the reaction coordinate is the angle φ between the Co—Co bond and one of the carbonyls of the $(CO)_4$ group. Isomer IVC is more stable than IVD, in accordance with the conclusion reached in ref. 14, and in line with the order of stability found for the non-bridged species of $Co_2(CO)_8$. A slight barrier was found in both isomers for the rotation around the Co—Co bond, the staggered conformer being favoured.

Direct calculation of the removal of a carbonyl from isomers IB and IC of $Co_2(CO)_8$ revealed that the departure of the equatorial CO takes place without any barrier in both cases, while a barrier of the order of 20 kcal/mol was found for removal of the axial CO from IC.

$HCo(CO)_4$. $HCo(CO)_4$ is stable in the gas phase at room temperature. Its structure has been the subject of much work and speculation [1], and recent

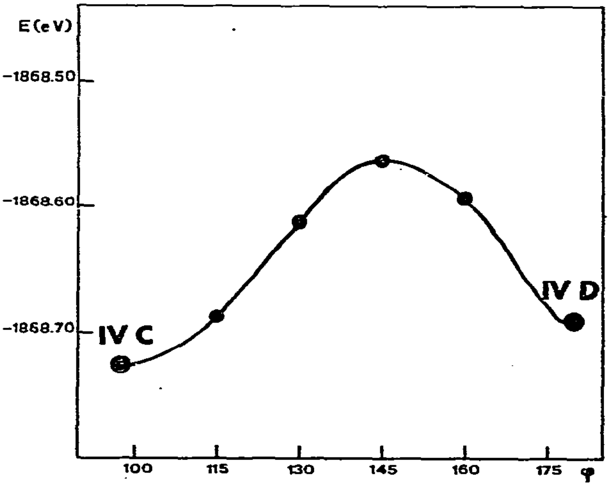

Fig. 4. Pathway for the interconversion process between the two isomers of $Co_2(CO)_7$. φ is the angle between the Co—Co bond and one of the carbonyls of the $Co(CO)_4$ group.

TABLE 3

GEOMETRICAL PARAMETERS FOR THE STRUCTURES OF THE COBALT CARBONYLS AND HYDROCARBONYLS

	Experimental			Calculated				
	Symmetry	ϑ [a]	Ref.	Symmetry	Structures	ϑ [a]	Ref.	E (eV)
$Co(CO)_3$	C_{3v}		13	C_s	IIIC	96°, 152°	[b, c]	—822.94
	D_{3h}		13	C_{3v} [d]	IIIA	105°	20	
				C_{2v} [d]	IIIB	105°, 150°	31 [c]	
$Co(CO)_4$	C_{3v}		13	D_{2d}	IIB	157°	[b]	—1043.94
	D_{2d}		13	D_{2d}	IIB	135°	20	
				D_{2d}	IIB	132°	31	
$Co(CO)_4^-$	T_d	109°28′	1	T_d		109°28′	[b]	—1057.50
$Co(CO)_4^{2-}$	T_d distorted		35	C_{3v}	IIA	107°	[b]	—1067.78
$HCo(CO)_3$				C_s	VIB	174°, 99°, 97°	[b, c]	—842.32
				C_{3v}	VIA	85°	[b]	—841.44
				C_{3v}	VIA	90°	5 [e]	
				C_{3v}	VIA	90°	5 [f]	
$HCo(CO)_4$	C_{3v}	87°	5 [g]	C_{3v}	VA	83°	[b]	—1062.81
	C_{3v}	80°18′	16	C_{4v}	VB	98°	[b]	—1062.50
	C_{3v}	79°	34	C_{3v}	VA	78°	20	
				C_{3v}	VA	90°	5 [e]	
				C_{4v}	VB	106°	5 [f]	
				C_{3v}	VA	83°30′	5 [f]	

[a] See in Fig. 1. [b] Present work: EHT calculations. [c] ϑ, ϑ', ϑ'' defined in Fig. 1. [d] Imposed. [e] "Ab initio" calculations. [f] CNDO calculations. [g] Average experimental value.

electron diffraction data [16] reveal a definite C_{3v} symmetry (VA) for it. Theoretical "ab initio" investigations [5,36] on its electronic structure were carried out. Another structure of higher symmetry, C_{4v} (VB), was also considered in a CNDO/2 approximation [5].

Our EHT calculations predict two isomers; the more stable of them has C_{3v} symmetry, in agreement with experimental data and the previous theoretical results. The path for the isomerization process has been studied by assuming $\varphi = C_{ax}CoH$ as reaction coordinate. The variation of E with φ is shown in Fig. 5, with an energy barrier of about 7 kcal/mol. A collection of experimental and theoretical geometry parameters is shown in Table 3.

Considerations of the reactivity of $HCo(CO)_4$ suggest that it may act as both a protonating and a reducing agent [1]. In the first case the reaction products are a proton and a tetrahedrally arranged $Co(CO)_4^-$ anion, while in the second case two neutral radicals are produced. On the basis of EHT calculations the two processes are energetically equivalent, and the T_d symmetry of $Co(CO)_4^-$ is confirmed.

$HCo(CO)_3$. $HCo(CO)_3$ has been suggested by several authors [1,3] to be the most probable catalyst in the hydroformylation reaction. Orchin et al. [37] recently reported experimental evidence for the existence of $HCo(CO)_3$ in matrix isolated $HCo(CO)_4$ after irradiation.

In previous calculations [5], the geometry of $HCo(CO)_3$, C_{3v} symmetry, was optimized by a CNDO and partly optimized by an "ab initio" technique (see

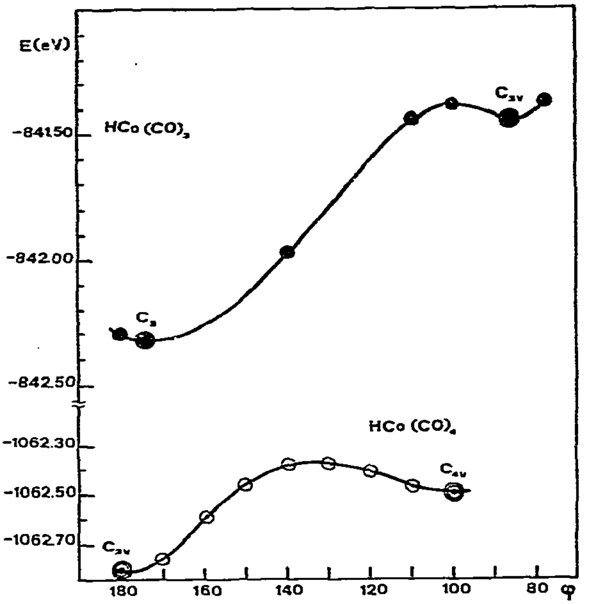

Fig. 5. Pathways for the interconversion processes of the stable isomers of $HCo(CO)_4$ and of $HCo(CO)_3$: φ is one of the HCoC angles.

Table 3). Our calculations point to the existence of two stable isomers, VIA and VIB in Fig. 1. The geometry of VIA is quite close to the C_{3v} structure mentioned above [5], while the latter, which appears to be the more stable, has C_s symmetry. A C_s symmetry could be allowed in terms of the number of C—O stretching bands assigned to $HCo(CO)_3$ [37].

The isomerization path from VIB to VIA is shown in Fig. 5, where the reaction coordinate φ is one of the HCoC angles. $HCo(CO)_3$ can be obtained from $HCo(CO)_4$ (VA) in two different ways: the removal of an equatorial carbonyl leads to the isomer VIB while the isomer VIA is obtained when the axial carbonyl is removed. In agreement with CNDO calculations [5], EHT results predict that the reactions occur without energy barriers.

Concluding remarks

In this paper attention has been focused on the geometries and the interconversion pathways of cobalt carbonyls and hydrocarbonyls, which proved to be effective catalysts in the "oxo" reactions [1,3,6]. Two points should be emphasized.

Firstly, within the limits of the predictive possibilities of the method, the EHT calculations provide interesting information on the structures of the stable isomers of cobalt carbonyls, as shown in Tables 2 and 3, and on the process of dissociation of $Co_2(CO)_8$, according to the following scheme:

$$\begin{tikzcd}
\mathrm{Co_2(CO)_8(I\ B)} \arrow[r, "1b"] \arrow[d, "1a"', "-\mathrm{CO}"] & 2\,\dot{\mathrm{C}}\mathrm{o(CO)_4(II\ B)} \arrow[d, "2b", "-\mathrm{CO}"'] \\
\mathrm{Co_2(CO)_7(IV\ C)} \arrow[r, "2a"] & \dot{\mathrm{C}}\mathrm{o(CO)_4} + \dot{\mathrm{C}}\mathrm{o(CO)_3(III\ C)}
\end{tikzcd}$$

ΔE(1a) 94 kcal/mol; ΔE(2a) 43 kcal/mol; ΔE(1B) 24 kcal/mol; ΔE(2b) 113 kcal/mol.

At a qualitative level it shows that $\dot{C}o(CO)_4$ radical species recombine with high efficiency [14], and in the light of this route 1a—2a must be preferred for the dissociation process. Secondly, with regard to the structure of the hydrocarbonyls, the stable isomers of $HCo(CO)_3$ deserve a special comment. A structure of C_s symmetry ($\vartheta = 174°$; $\vartheta' = 99°$; $\vartheta'' = 97°$), as shown in Fig. 1 and Table 3, is predicted for the more stable isomer. Such a geometry is very interesting and would account for the formation of the π-allyl type complex with the olefin which is indicated by experiment [1,3]. On the whole it appears that the EHT calculations provide a consistent rationale for the existence of stable isomers of cobalt carbonyls and hydrocarbonyls, and give unambiguous information on their geometries. In the light of this calculations on catalysts involving different transition metals are in progress. On the other hand more refined "ab initio" calculations are preferable to give information about reaction mechanisms.

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References

1 M. Orchin and W. Rupilius, Catal. Rev., 6 (1972) 85.
2 F.F. Seelig, Z. Naturforsch. B, 31 (1976) 336.
3 P. Pino, F. Piacenti and M. Bianchi, in I. Wender and P. Pino (Eds.), Organic Syntheses via Metal Carbonyls, Vol. II, Wiley, New York, 1977, p. 43—215.
4 D.L. Lichtenberger and T.L. Brown, Inorg. Chem., 17 (1978) 1381.
5 J.Ph. Grima, F. Choplin and G. Kaufmann, J. Organometal. Chem., 129 (1977) 221.
6 P. Pino, R. Ercoli and F. Calderazzo, Chim. Ind. (Milan), 37 (1955) 782.
7 F. Ungváry, J. Organometal. Chem., 36 (1972) 363.
8 G. Bor and K. Noack, J. Organometal. Chem., 64 (1974) 367.
9 G. Bor, U.K. Dietler and K. Noack, J. Chem. Soc., Chem. Commun., (1976) 914.
10 G. Bor and U.K. Dietler, IXth Intern. Conf. Organometal. Chem., Dijon, Sept. 1979.
11 S. Onaka and D.F. Shriver, Inorg. Chem., 15 (1976) 915.
12 R.L. Sweany and T.L. Brown, Inorg. Chem., 16 (1977) 415.
13 L.A. Hanlan, H. Huber, E.P. Kündig, B.R. McGarvey and G.A. Ozin, J. Amer. Chem. Soc., 97 (1975) 7054.
14 R.L. Sweany and T.L. Brown, Inorg. Chem., 16 (1977) 421.
15 G. Gardner Sumner, H.P. Klug and L.E. Alexander, Acta Crystallogr., 17 (1964) 723.
16 E.A. McNeill and F.R. Scholer, J. Amer. Chem. Soc., 99 (1977) 6243.
17 S.A. Fieldhouse, B.W. Fullam, G.W. Neilson and M.C.R. Symons, J. Chem. Soc., Dalton Trans., (1974) 567.
18 R. Hoffmann, J. Chem. Phys., 39 (1963) 1397.
19 A.R. Rossi and R. Hoffmann, Inorg. Chem., 14 (1975) 365.
20 M. Elian and R. Hoffmann, Inorg. Chem., 14 (1975) 1058.
21 A.B. Anderson, Inorg. Chem., 15 (1976) 2598.
22 D.L. Thorn and R. Hoffmann, Inorg. Chem., 17 (1978) 126.
23 R.P. Messmer, S.K. Knudson, K.H. Johnson, J.B. Diamond and C.Y. Yang, Phys. Rev. B., 13 (1976) 1396.
24 A.B. Anderson, J. Chem. Phys., 68 (1978) 1744.

25 C. Bachmann, J. Demuynck and A. Veillard, Gazz. Chim. Ital., 108 (1978) 389.
26 M. Wolfsberg and L. Helmholz, J. Chem. Phys., 20 (1952) 837.
27 L.L. Lohr Jr. and W.N. Lipscomb, Inorg. Chem., 3 (1964) 22.
28 M.J.D. Powell, Computer J., 7 (1964) 155.
29 P.J. Gardner, A. Cartner, R.G. Cunninghame and B.H. Robinson, J. Chem. Soc. Dalton Trans., (1975) 2582.
30 J.A. Connor, M.A. Skinner and Y. Virmani, Faraday Symp., Chem. Soc., 8 (1973) 18.
31 J.K. Burdett, J. Chem. Soc. Faraday Trans. II, 70 (1976) 1599.
32 F. Ungváry and L. Markó, Inorg. Chim. Acta, 4 (1970) 324.
33 F. Ungváry and L. Markó, J. Organometal. Chem., 71 (1974) 283.
34 G. Bor, Inorg. Chim. Acta, 1 (1967) 82.
35 M.C.R. Symons and D.M. Zimmerman, J. Chem. Soc., Dalton Trans., (1975) 2545.
36 N. Fonnesbech, J. Hjortkjaer and H. Johansen, Int. J. Quantum Chem., 12 (Suppl. 2) (1977) 95.
37 P. Wermer, B.S. Ault and M. Orchin, J. Organometal. Chem., 162 (1978) 189.