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# An MO-theoretical Interpretation of the Reductive Cleavage of Organic Halides by Pentacyanocobaltate(II)

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The mechanism of the reductive cleavage of organic halides (RX) by pentacyanocobaltate(II) $Co(CN)_5^{3-}$ was investigated by means of the extended Hückel MO theory. First, the molecular structure of $Co(CN)_5^{3-}$ was considered to be the square-pyramidal $C_{4v}$ configuration, without $H_2O$ as its sixth ligand. Secondly, the order of the observed rate constants for the $Co(CN)_5^{3-}+RX \rightarrow Co(CN)_5X^{3-}+R\cdot$ reaction was found to be in satisfactory accordance with that of the calculated binding energies of the R–X bond. Thirdly, the reductive cleavage of RX by $Co(CN)_5^{3-}$ proceeds by the aid of the predominant electron-migration from the highest-occupied, lone-pair halogen-orbital to the singly-occupied $d_{z^2}$ Co-orbital and from the highest-occupied $d_{xz}$ (or $d_{yz}$) Co-orbital to the lowest-unoccupied, antibonding $p\sigma^*$ orbital of the R–X bond. Finally, the mode of the interaction between $Co(CN)_5^{3-}$ and RX was precisely discussed in terms of the homolytic cleavage of the R–X bond.

It has been well established that organocobalt compounds can be easily formed by the reductive cleavage of organic halides with pentacyanocobaltate(II)[1–6]:

$$2Co(CN)_5^{3-} + RX \rightarrow Co(CN)_5R^{3-} + Co(CN)_5X^{3-} \quad (1)$$

The mechanism of such a reaction has been interpreted mainly, by the kinetic and other studies of Halpern *et al.*,[2,3,6] in terms of the free-radical reaction according to:

$$Co(CN)_5^{3-} + RX \rightarrow$$
$$Co(CN)_5X^{3-} + R\cdot \quad \text{(rate-determining)} \quad (2)$$
$$Co(CN)_5^{3-} + R\cdot \rightarrow Co(CN)_5R^{3-} \quad (3)$$

Since any precise discussion referred to the above reactions, however, depends in the early stages on a molecular level, molecular orbital study seems significant.

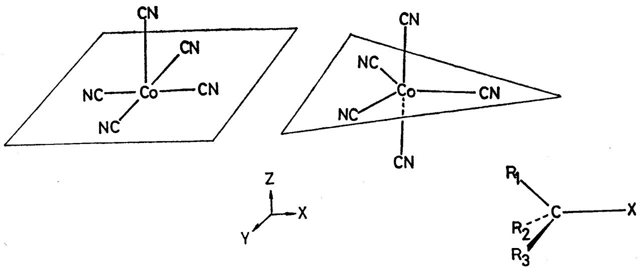
The present study was undertaken in order to elucidate the mechanism of the reductive cleavage of RX by $Co(CN)_5^{3-}$, using throughout the extended Hückel MO method, with particular reference to the plausible model of the interaction between the two compounds.

## Method of Calculation

An extended Hückel MO (EHMO) method[7] involving metal d-orbitals was used for the calculations on the following three systems:

(a) pentacyanocobaltate(II): square-pyramidal $C_{4v}$ and trigonal-bipyramidal $D_{3h}$ $Co(CN)_5^{3-}$, (b) organic halides: RI (R=$CH_3$, $C_2H_5$, *i*-$C_3H_7$, and *t*-$C_4H_9$), $XCH_2CO_2CH_3$ and $XCH_2CONH_2$ (X=Cl, Br, and I), and (c) an interacting system of $Co(CN)_5^{3-}$ and RX ($CH_3I$ was tentatively taken).

The orbital exponents and ionization energies for the s and p orbitals of the C, N, O, and halogen atoms were supplied by Clementi[8] and by Jaffé[9] respectively. The ionization energies for the s, p, and d orbitals of the Co atom were, respectively, taken to be 10.0 eV,[10] 8.0 eV,[10] and 11.0 eV.[10]



Co-C=2.30–1.50 Å
C-N=1.30 Å

C-Cl=1.767 Å
C-Br=1.939 Å
C-I=2.139 Å

Fig. 1. Geometries of pentacyanocobaltate(II) and organic halides used for the calculation.

The geometries used for the calculations are illustrated in Fig. 1; the interatomic distance and the valence angles for $XCH_2CO_2CH_3$ and $XCH_2CONH_2$ were determined uniformly from those[12] of $CH_3CO_2CH_3$ and $CH_3CONH_2$, with the fixed angle of C–C–X (109°28′), for the sake of simplicity.

## Results and Discussion

*Molecular Structure of* $Co(CN)_5^{3-}$. The molecular structure of $Co(CN)_5^{3-}$ in solution has not yet been strictly established; the square-pyramidal $C_{4v}$ $Co(CN)_5^{3-}$ has been predominantly discussed as compared with the trigonal-bipyramidal $D_{3h}$ one.

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[1] J. Halpern and J. P. Maher, *J. Amer. Chem. Soc.*, **86**, 2311 (1964).

[2] J. Halpern and J. P. Maher, *ibid.*, **87**, 5361 (1965).

[3] J. Kwaitek and J. K. Seyler, *J. Organometal. Chem.*, **3**, 421 (1965).

[4] J. Kwiatek and J. K. Seyler, *Advance in Chemistry Series*, No. 70, American Chemical Society, Washington, D. C. (1968), p. 207.

[5] J. Kwiatek, *Catalysis Rev.*, **1**, 37 (1967).

[6] P. B. Chock and J. Halpern, *J. Amer. Chem. Soc.*, **91**, 582 (1969).

[7] K. Ohkubo and H. Kanaeda, *J. Chem. Soc. Faraday Trans. II*, **68**, 1164 (1972); For the basic principles, see R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963); *ibid.*, **40**, 2474 (1964).

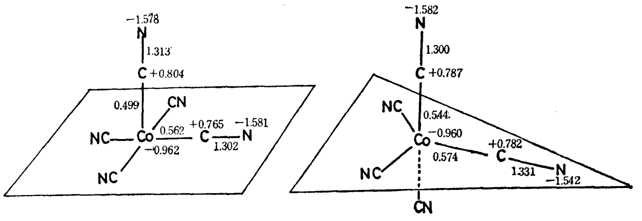
[8] E. Clementi and D. L. Raimondi, *J. Chem. Phys.*, **38**, 2686 (1963).

[9] J. Hinze and H. H. Jaffé, *J. Amer. Chem. Soc.*, **84**, 540 (1962).

[10] L. L. Lohr, Jr., and W. W. Lipscomb, *Inorg. Chem.*, **3**, 22 (1964). Another values of the ionization energies, for the s, p, and d Co-orbitals, such as 5.66 eV,[11] and 7.84 eV[11] respectively, were found to be unsuitable for the present calculations on $Co(CN)_5^{3-}$, because in the calculations with the above parameters, Co was much positively charged and the bond population of Co–C was negatively calculated.

[11] F. A. Cotton and T. E. Haas, *ibid.*, **3**, 1004 (1964).

[12] L. E. Sutton, Editor, "Interatomic Distances," The Chemical Society, London (1958).



$C_{4v}$ $E_{EH} = -1009.116$ eV

$D_{3h}$ $E_{EH} = -1009.770$ eV

Fig. 2. Electronic structures of $C_{4v}$ and $D_{3h}$ $Co(CN)_5^{3-}$.

We will first discuss which structure, the $C_{4v}$ or the $D_{3h}$, is more likely for $Co(CN)_5^{3-}$. Fig. 2 shows the formal charges ($Q_A$), the bond populations ($M_{A-B}$), and the total electronic energies ($E_{EH}$) of $C_{4v}$ and $D_{3h}$ $Co(CN)_5^{3-}$ at a fixed Co–C distance of 1.81 Å.[13] As Fig. 2 indicates, the electronic structures of the $C_{4v}$ and the $D_{3h}$ $Co(CN)_5^{3-}$ resemble each other, since they have almost the same values of $Q_A$, $M_{A-B}$, and $E_{EH}$.

According to the $E_{EH}$ values of the $C_{4v}$ and $D_{3h}$ $Co(CN)_5^{3-}$ at the Co–C distances of 1.5∼2.3 Å (Table 1), the latter cobaltate seems to be slightly more stable than the former. The energy difference between the two cobaltates is, however, quite small; that is, it is difficult to conclude the stability of the trigonal-pyramidal $D_{3h}$ structure for $Co(CN)_5^{3-}$ from the total energy, neglecting the electron-electron and nuclear-nuclear repulsions.

On the other hand, the 10 Dq value estimated from the energy difference between the lowest-unoccupied (LU) and the singly-occupied (SO) orbitals[14] of the Co atom offers some information about the molecular structure of $Co(CN)_5^{3-}$. The 10 Dq value for the $C_{4v}$ $Co(CN)_5^{3-}$, 32.09 kK, at the Co–C distance of 1.81 Å was found to be in good agreement with that of 33 kK obtained experimentally by Caulton.[15]

Since the $C_{4v}$ structure was demonstrated by Alexander and Gray[16] in their ESR and UV spectroscopic investigations of $Co(CN)_5^{3-}$, and since the theoretical values of 10 Dq agree with those in the experiments, the square-pyramidal $C_{4v}$ $Co(CN)_5^{3-}$ seems to be more likely than the trigonal-pyramidal $D_{3h}$ one, and the Co–C distance seems to be about 1.81 Å.

On the other hand, there have been some discussions[17] referred to $Co(CN)_5^{3-}$ coordinated by $H_2O$ as its sixth ligand in aqueous solutions. According to the calculated results of the $C_{4v}$ $Co(CN)^{3-}$, $H_2O$, and octahedral $Co(CN)_5OH_2^{3-}$ (Co–O was taken to be 1.93 Å,[18] the isolated systems of $Co(CN)_5^{3-}$ and $H_2O$ (the sum of their $E_{EH}$ values $= -1169.72$ eV) can be said to be energetically more stable than $Co(CN)_5OH_2^{3-}$ ($E_{EH} = -1167.96$ eV). It may be deduced, therefore, that $H_2O$ does not coordinate directly to $Co(CN)_5^{3-}$.

Here, the bond nature of the $C_{4v}$ $Co(CN)_5^{3-}$ will be discussed briefly. Table 2 lists the AO bond populations ($N_{A-B}$) of the Co–C and C–N bonds. The d Co-orbitals contribute mainly to the dp-π-type bond

TABLE 1. TOTAL ELECTRONIC ENERGIES OF $C_{4v}$ AND $D_{3h}$ $Co(CN)_5^{3-}$

| | $Co(CN)_5^{3-}$ geometry | 1.50 Å | 1.81 Å | 2.30 Å |
|---|---|---|---|---|
| $E_{EH}$(eV) | $D_{3h}$ | −1013.015 | −1009.770 | −1006·616 |
| | $C_{4v}$ | −1012.333 | −1009.116 | −1006.217 |
| Nuclear-nuclear repulsion (eV) | $D_{3h}$ | 7516.707 | 6821.210 | 5938.764 |
| | $C_{4v}$ | 7606.707 | 6821.210 | 5938.764 |
| 10Dq (kK) | $D_{3h}$ | 29.77 | 18.88 | 3.47 |
| | $C_{4v}$ | 126.3 | 33.04 | 3.19 |

TABLE 2. BOND POPULATIONS OF Co-C AND C-N[a)]

| Bond | σ Overlap | σ $N_{Co-C}$ | π Overlap | π $N_{Co-C}$ |
|---|---|---|---|---|
| Co-C | s-s | 0.0476 | $p_y$-$p_y$ | 0.0178 |
| | s-$p_x$ | 0.0430 | $p_z$-$p_z$ | 0.0462 |
| | $p_x$-$p_x$ | 0.0899 | $d_{xz}$-$p_z$ | 0.0381 |
| | $p_x$-s | 0.1442 | $d_{xy}$-$p_y$ | 0.0376 |
| | $d_{x^2-y^2}$-s | 0.0317 | $d_{z^2}$-$p_z$ | 0.0067 |
| | total | 0.4225 | total | 0.1464 |

| Bond | σ Overlap | σ $N_{C-N}$ | π Overlap | π $N_{C-N}$ |
|---|---|---|---|---|
| C-N | s-s | 0.1701 | $p_y$-$p_y$ | 0.2471 |
| | s-$p_x$ | 0.2432 | $p_z$-$p_z$ | 0.2443 |
| | $p_x$-$p_x$ | 0.1744 | | |
| | $p_x$-s | 0.2226 | | |
| | total | 0.8103 | total | 0.4914 |

a) Co-CN bond on x-axis.

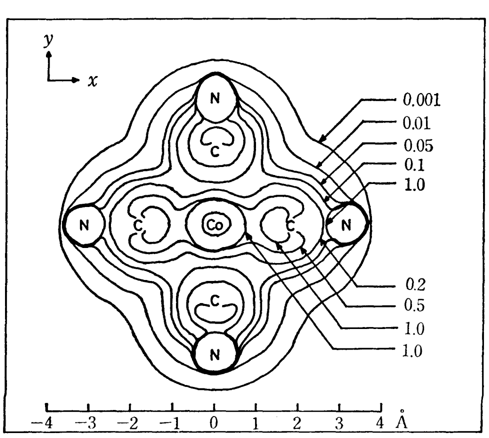


Fig. 3. Charge density contour of $C_{4v}$ $Co(CN)_5^{3-}$. (The representation is in xy cross section.)

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[13] Lipscomb *et al.*[10] emphasized the Co–CN distance of 1.81 Å by their study on $Co(CN)_5H^{3-}$.

[14] The LUMO and the SOMO are, respectively, $d_{x^2-y^2}$ and $d_{z^2}$ orbitals for the $C_{4v}$ $Co(CN)_5^{3-}$ and are, respectively, $d_{z^2}$ and $d_{xy}$ orbitals for the $D_{3h}$ $Co(CN)_5^{3-}$.

[15] K. G. Caulton, *Inorg. Chem.*, **7**, 392 (1968).

[16] J. J. Alexander and H. B. Gray, *J. Amer. Chem. Soc.*, **89**, 3356 (1967).

[17] For instance, see J. M. Pratt, and R. J. P. Williams, *J. Chem. Soc., Ser.* A, **1967**, 1291.

[18] The purely covalent bond-distance was used because the usual bond-distances of metal-oxygen in aquo-complexes are purely covalent (see Ref. 12).

TABLE 3. CORRELATION BETWEEN THE ELECTRONIC PROPERTIES AND REACTIVITIES OF RX AND THE $k_{obs}$ VALUES FOR THE REACTION, $RX + Co(CN)_5^{3-} \rightarrow R\cdot + Co(CN)_5X^{3-}$

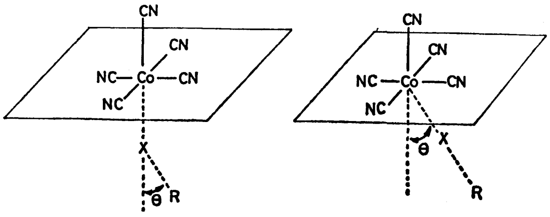
| RX | $k_{obs}$[a] ($M^{-1}\,s^{-1}$) | $D_{298}$[b] (kcal/mol) | Binding[c] energy (kcal/mol) | $M_{C-X}$ | $N_{p\sigma}$ | $N_{lone-pair}$ |
|---|---|---|---|---|---|---|
| $CH_3I$ | $9.5\times10^{-3}$ | 56.0 | 60.88 | 0.5107 | 0.3435 | 1.9995 |
| $C_2H_5I$ | $5.9\times10^{-2}$ | 53.0 | 58.40 | 0.580 | 0.3384 | 1.9990 |
| $i$-$C_3H_7I$ | 1.2 | 50.0 | 54.11 | 0.5153 | 0.3319 | 1.9987 |
| $t$-$C_4H_9I$ | 9.1 | 50.0 | 53.24 | 0.5197 | 0.3285 | 1.9983 |
| $ClCH_2CO_2CH_3$ | $\sim10^{-3}$ | | 28.05 | 0.6030 | 0.3648 | 1.9965 |
| $ClCH_2CONH_2$ | $\sim6\times10^{-4}$ | | 32.28 | 0.6266 | 0.3638 | 1.9934 |
| $BrCH_2CO_2CH_3$ | $\sim34$ | | 37.68 | 0.5980 | 0.3862 | 1.9977 |
| $BrCH_2CONH_2$ | 16.4 | | 40.61 | 0.6218 | 0.3845 | 1.9948 |
| $ICH_2CO_2CH_3$ | $8.8\times10^{4}$ | | 55.71 | 0.5037 | 0.3417 | 1.9988 |
| $ICH_2CONH_2$ | $2.95\times10^{4}$ | | 62.43 | 0.5190 | 0.3419 | 1.9975 |

a) 1:1 methanol-water by volume at 25°C for $XCH_2CO_2CH_3$ and $XCH_2CONH_2$, and 2:8 water-methanol at 25°C for RI. Cited from Refs. 2 and 6. b) Quoted from J. A. Kerr, *Chem. Rev.*, **66**, 465 (1966). c) Binding energy $= |E_{EH}(RX) - (E_{EH}(R\cdot) + E_{EH}(X\cdot))|$.

TABLE 4. BOND POPULATIONS OF C-I IN VARIOUS MODES OF INTERACTION BETWEEN $CH_3I$ AND $Co(CN)_5^{3-}$

| Type of interaction | θ, (deg.) | Bond population of C-I | | |
|---|---|---|---|---|
| | | Initial | Transition | Final[a] |
| A | 0 | 0.5065 | 0.1237 | −0.0057 |
| | 30 | 0.5.73 | 0.1251 | −0.0001 |
| | 45 | 0.5082 | 0.1281 | 0.3104 |
| | 60 | 0.5089 | 0.1413 | 0.0045 |
| | 90 | 0.5090 | 0.1455 | 0.0082 |
| B | 12 | 0.5065 | 0.1215 | −0.0053 |
| | 22.5 | | 0.1160 | −0.0050 |
| | 33 | 0.5051 | 0.1081 | −0.0046 |
| | 45 | 0.5011 | 0.1005 | −0.0031 |

a) Co-I=3.60 Å, C-I=2.139 Å, and ∠HCI=109°28′ for the initial system, Co-I=2.90 Å, C-I=2.82 Å, and ∠HCI=99°44′ for the transition system, and Co-I=2.52 Å, C-I=3.50 Å, and ∠HCI=90° for the final system.



Type A Type B

TABLE 5. ELECTRON DENSITIES OF I IN $CH_3I$ AND Co IN $Co(CN)_5^{3-}$ IN THEIR VARIOUS STATES

| Atom | Orbital | Electron densities | | | | | |
|---|---|---|---|---|---|---|---|
| | | $CH_3I$[a] | $CH_3I$[b] | $Co(CN)_5^{3-}$ [c] | Initial[d] | Transition[d] | Final[d] |
| I | s | 1.8207 | 1.9731 | | 1.8046 | 1.7657 | 1.6344 |
| | $p_x$ | 1.3582 | 1.5690 | | 1.3025 | 1.2714 | 1.4452 |
| | $p_y$ | 1.9995 | 1.9999 | | 1.9967 | 1.9496 | 1.8324 |
| | $p_z$ | 1.9995 | 1.9999 | | 1.9948 | 1.6552 | 1.2559 |
| Co | $d_{xz}$ | | | 1.5844 | 1.6068 | 1.4552 | 1.2878 |
| | $d_{yz}$ | | | 1.5844 | 1.5848 | 1.5909 | 1.6063 |
| | $d_{xy}$ | | | 1.3491 | 1.3507 | 1.3827 | 1.4657 |
| | $d_{x^2-y^2}$ | | | 1.1621 | 1.1696 | 1.1523 | 1.1262 |
| | $d_{z^2}$ | | | 0.9511 | 0.9805 | 1.2595 | 1.0930 |

a) In the geometry of the initial state (see Fig. 1).
b) In the geometry of the transition state (see Table 4).
c) In the geometry of the initial state (see Fig. 1).
d) Interacting system between $CH_3I$ and $Co(CN)_5^{3-}$, and the geometries were shown in Table 4.

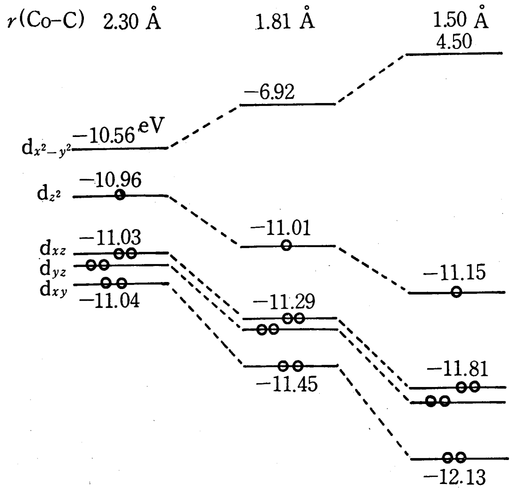


Fig. 4. d-Orbital separation of $C_{4v}$ $Co(CN)_5^{3-}$ as a function of Co–C distance.

formation of the Co–C bond, and the $d_{x^2-y^2}$ Co-orbital takes part in the ds-$\sigma$-type bond formation of the Co–C in some measure. The net charge-density contour for the $C_{4v}$ $Co(CN)_5^{3-}$ is illustrated in Fig. 3 to facilitate an understanding of the bond nature discussed above and the electron distribution of the compound.

*Frontier Orbitals of $Co(CN)_5^{3-}$ and RX.* The d-orbital separation on the Co atom of the $C_{4v}$ $Co(CN)_5^{3-}$ is shown in Fig. 4; the cobaltate is characterized by the SO $d_{z^2}$ and the doubly-degenerate, highest occupied (HO) $d_{xz}$ and $d_{yz}$ Co-orbitals. On the other hand, the frontier orbitals of RX are the doubly-degenerate, HO lone-pair $p_z$ and $p_y$ orbitals on X and the antibonding, LU $p\sigma^*$ orbital on the C–X axis. It seems certain that the above-mentioned orbitals corresponding to the frontier MOs play an important role in the reductive cleavage of RX by $Co(CN)_5^{3-}$: The SOMO (and/or the HOMO) of $Co(CN)_5^{3-}$ interacts predominantly with the LUMO, the HOMO, or both the MOs of RX respectively in the nucleophilic, electrophilic, or radical attack of the former on the latter.

*Correlation between the Electronic States of RX and the Reaction Rates for $Co(CN)_5^{3-}+RX\rightarrow Co(CN)_5X^{3-}+R\cdot$.* In this section, we will discuss the correlation between the bond nature of RX and the observed rate constants, $k_{obsd}$, for Eq. (2) (see Introduction). As can be seen from Table 3, the order of $k_{obsd}$ values is satisfactorily reflected in that of the dissociation energies, $D_{298}$ (in other words, binding energies or $M_{C-X}$ values). On the other hand, no parallelism between the order of the AO-bond population of the $p\sigma$-orbitals on the C–X axis ($N_{p\sigma}$) or of the lone-pair $p_z$-orbital on X ($N_{lone-pair}$) and that of the $k_{obsd}$ values can be consistently realized between the two series of RI and $XCH_2CO_2CH_3$ and/or $XCH_2CONH_2$; that is, the order of the $k_{obsd}$ values cannot be explained by only that of the $N_{p\sigma}$ or $N_{lone-pair}$ values. It can be deduced, therefore, that both the $p\sigma^*$ C–X orbital and the lone-pair X-orbital take part directly in the interaction with $Co(CN)_5^{3-}$.

*Interacting System of $Co(CN)_5^{3-}$ and RX.* We will here determine the most plausible mode of the interaction between $Co(CN)_5^{3-}$ and RX in terms of the homolytic cleavage of the R–X bond. The EHMO calculations were performed on the two modes of interaction between $Co(CN)_5^{3-}$ and RX ($CH_3I$ was tentatively used), *i.e.*, Type-A and Type-B, both illustrated in Table 4.

It may be found from Table 4 that the C–I bond of $CH_3I$ is most weakened by the Type-B interaction at $\theta=45°$ in view of the fact that the $M_{C-I}$ values of such interaction are the smallest throught the reaction progress. The Type-B interaction at $\theta=45°$ seems to be the most appropriate interacting form in which plausible overlappings between the frontier orbitals of both compounds can be established (see Fig. 5).

With regard to the electron migrations between $Co(CN)_5^{3-}$ and RX, the migrations depicted by Eqs. (4)∼(7) can be considered on the basis of the changes in the electron densities of the s and p X-orbitals and the d Co-orbitals, as is indicated in Table 5:

$$p_z^{(X)}\ (\text{lone-pair}) \xrightarrow{\text{through } d_{z2}{}^{(Co)}-p_z{}^{(X)}} d_{z^2}{}^{(Co)}\ (\text{predominant}) \tag{4}$$

$$p_y{}^{(X)}\ (\text{lone-pair}) \xrightarrow{\text{through } d_{yz}{}^{(Co)}-p_y{}^{(X)}} d_{yz}{}^{(Co)} \tag{5}$$

$$\searrow \xrightarrow{\text{through } d_{xy}{}^{(Co)}-p_y{}^{(X)}} d_{xy}{}^{(Co)} \tag{6}$$

$$d_{xz}{}^{(Co)} \xrightarrow{\text{through } d_{xz}{}^{(Co)}-p_x{}^{(X)}} p_x{}^{(X)}\ (\text{predominant}) \tag{7}$$

The predominant electron-migrations depicted by Eqs. (4) and (7) bring about, respectively, the decrease in the bonding character of the R–X and the increase in the antibonding character of the same bond, as may be seen from the energy-change in the frontier orbital levels of RX (*viz.* $CH_3I$) in Fig. 5.

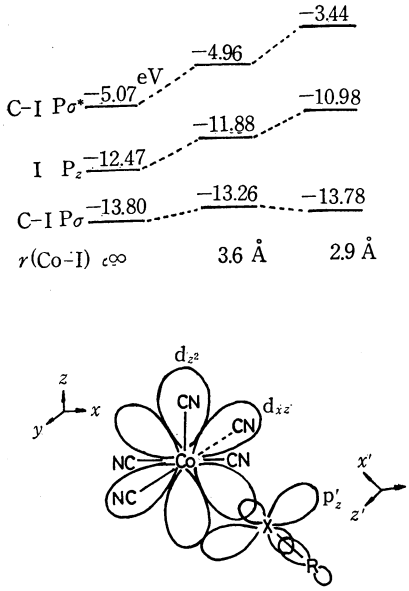


Fig. 5. MO-energy changes in frontier orbitals of RX by optimized interaction of $Co(CN)_5^{3-}$.

The present calculations were carried out on a FACOM 230-60 computer at the Data Processing Center of Kyushu University.