Spectroscopic and Theoretical Studies of Charge-Transfer Type Molecular Complexes between Monoölefins and Metal Ions: Selective Complex Formation Abilities of Copper(I), Silver(I) and Mercury(II) Ions

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Since Mulliken[1] developed the quantum-mechanical concept of the electron donor and acceptor with relation to the mechanism of molecular complex formation, both experimental and theoretical studies have been successively and successfully accomplished by many authors.[2] Rather little, however, is known about molecule-ion type complexes, such as the silver cation complexes with olefins and aromatic hydrocarbons; many problems are yet unsolved for this type of molecular complexes. Some of them are as follows:

i) Among the closed shell-type metal ions, why can only the copper(I), silver(I) and mercury(II) ions form stable complexes with monoölefins ?[3,4]

ii) To what extent do the d-orbital electrons of these ions play a role in the complex formation,[5] and what kind of role is it ?

iii) Do these monoölefin-metal ion complexes really show charge-transfer absorption bands ?[6-8]

iv) Counter negative ions of silver salts affect the stability of the monoölefin-silver ion complexes. That is, the stability decreases in the order of $AgClO_4 > AgNO_3 \gg AgCl$, Ag_2SO_4.[7,8] How do we explain the difference in stability ?

v) Is there any relation between the olefin-silver ion complex and the olefin-bromonium ion complex, which is known to be a reaction intermediate for the bromine addition reaction ?[9]

The aim of the present study is to settle some of these problems as definitely as possible. In order to accomplish this purpose, we undertook to measure the ultraviolet, infrared and Raman spectra of the cyclohexene-silver perchlorate complex under various conditions, and to carry out some theoretical studies of the electronic energy levels of the complex. Furthermore, the stability of monoölefin-metal ion complexes will be discussed in detail in connection with the solvation energies of various metal ions.

Experimental

Materials. — Cyclohexene was distilled from cyclohexanol over a small amount of concentrated sulfuric acid. The distillate was dried with sodium metal and purified by repeating fractional distillation. Silver perchlorate of E. P. grade was used without further purification, since the infrared spectrum showed no marked difference between the cyclohexene complex with silver perchlorate recrystallized from acetone and that with the commercial silver perchlorate. Silver chloride precipitated from the mixture of aqueous silver nitrate and sodium chloride was dried over phosphorus pentoxide in the dark. Anhydrous cadmium perchlorate was synthesized from cadmium carbonate and perchloric acid, followed by dehydration at 100°C in vacuo.[10] Commercial silver nitrate, silver sulfate, potassium perchlorate, sodium perchlorate and magnesium perchlorate were used without further purification.[11]

Methanol, ethanol and tetrahydrofuran used as solvents were purified according to the standard methods.[12,13] Deuterated water (99.8%) was purchased from Asahi Kasei Co.

The cyclohexene-silver perchlorate complex was obtained by mixing the component substances directly and was recrystallized from ethanol.[14]

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1) R. S. Mulliken, *J. Chem. Phys.*, **56**, 801 (1952).

2) G. Briegleb, "Elektronen-Donator-Acceptor-Komplexe," Springer-Verlag, Berlin (1961).

3) S. Winstein and H. J. Lucas, *J. Am. Chem. Soc.*, **60**, 836 (1938); H. J. Lucas, F. R. Hepner and S. Winstein, ibid., **61**, 3102 (1939).

4) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley & Sons Inc., New York (1958), p. 351.

5) M. J. S. Dewar, *Bull. soc. chim. France*, **1951**, C71; *J. Chem. Soc.*, **1946**, 406, 777; *Discussions Faraday Soc.*, **2**, 151 (1947).

6) R. S. Mulliken, *J. Am. Chem. Soc.*, **74**, 811 (1952); *J. Chem. Phys.*, **19**, 514 (1951).

7) G. Salomon, "Cationic Polymerisation and Related Complexes," Ed. by P. H. Plesch, Academic Press, New York (1953), p. 57.

8) L. E. Orgel, *Quart. Revs.*, **8**, 422 (1954).

9) J. W. Kraus and E. W. Stern, *J. Am. Chem. Soc.*, **84**, 2893 (1962).

10) H. Hering and A. Leray, *Bull. soc. chim. France*, **6**, 1034 (1939).

11) Cyclohexene was found immissible with aqueous $KClO_4$, $NaClO_4$, $Mg(ClO_4)_2$ and $Cd(ClO_4)_2$. The white crystals of cyclohexene-silver perchlorate were soluble in methanol, ethanol and tetrahydrofuran, but were insoluble in water, carbon tetrachloride and *n*-heptane. The mixture of cyclohexene with acetonitrile or concentrated sulfuric acid became turbid. The cyclohexene-silver perchlorate complex became yellowish the moment it came in contact with potassium bromide, indicating decomposition into silver bromide.

12) A. Weissberger and E. Proskauer, "Organic Solvents," Oxford University Press, Oxford (1935), pp. 114, 118.

13) A. Ishitani, K. Kuwata, H. Tsubomura and S. Nagakura, This Bulletin, **36**, 1357 (1963).

14) A. E. Comyns and H. J. Lucas, *J. Am. Chem. Soc.*, **79**, 4339 (1957).

The cyclohexene-silver nitrate complex was crystallized from an ethanol solution of cyclohexene and silver nitrate at 0°C.[14]

Measurements of Ultraviolet Absorption Spectra. —A Cary recording spectrophotometer model 14 M was used for measuring ultraviolet spectra, fused quartz cells of 1 mm. light-path length being used. All the measurements were carried out at a constant temperature (20°C). The relatively strong absorption of the silver ion prevents us from measuring the spectra of solutions with concentrations higher than 0.1 N. The spectrum of cyclohexene was measured in aqueous silver perchlorate solutions with various concentrations and in a relatively concentrated aqueous cadmium perchlorate solution.

Measurements of Infrared and Raman Spectra. —A Hitachi EPI-2 infrared spectrophotometer, with a rock salt prism attached, was used for the infrared absorption measurements. Some of the solution spectra in the regions of 6 μ and 14 μ were measured with polyethylene bags. An envelope ca. 20×30 mm² was made from two sheets of polyethylene film 0.08 mm. thick, with no adhesive reagent but with moderate heating. The bag was then filled with a liquid sample and held by a commercial cell-window holder more or less tightly in order to avoid the wrinkling of the film and the vaporization of the solvent.

Raman spectra were measured with a Cary recording Raman spectrophotometer model 81 located at the Government Chemical Industrial Research Institute.[15]

Experimental Result for the Cyclohexene-Silver Perchlorate Complex

The Ultraviolet Absorption Spectrum of the Complex. — The absorption spectra measured with the cyclohexene-silver perchlorate-water system are shown in Fig. 1, whose ordinate represents the apparent molar extinction coefficients, ε's, the definition of which will be given later. As may be seen in Fig. 1, the ultraviolet absorption spectrum of cyclohexene in an aqueous silver perchlorate solution gradually but definitely increases its intensity with the increment of the salt concentration; in spite of less accuracy partly because of the relatively strong absorption of silver perchlorate ($\varepsilon=800$ at $\lambda_{\max}=210$ mμ). This absorption change clearly shows that a new band appears at 220～230 mμ for the cyclohexene-silver perchlorate-water system. On the other hand, the spectrum of cyclohexene in an aqueous solution of 2 N cadmium perchlorate, like that of free cyclohexene, shows no absorption band above 220 mμ.

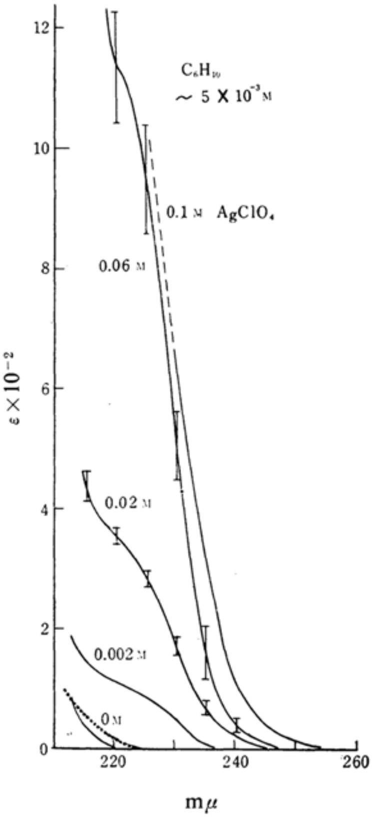

Fig. 1. Ultraviolet absorption spectra of cyclohexene in aqueous solutions of various concentrations of silver perchlorate (——) and of 1 mol./l. cadmium perchlorate (……). Vertical lines represent the possible errors due to absorption by aqueous silver perchlorate solutions.

From a consideration of the equilibrium constant described below, we can safely conclude that the new band at about 220～230 mμ is due to the one-to-one complex of monoölefin and silver salt. This seems to mean that we could find Mulliken's[6] charge-transfer absorption band, which Salomon[7] and others[8] were unable to find for this system. Further details on the nature of this band will be discussed in a later part of the present paper.

Let us make a rough estimation of the equilibrium constant, K, for the system;

$$C_6H_{10} + AgClO_4 \rightleftharpoons C_6H_{10}\cdots Ag^+ClO_4^-$$

$$d-x \qquad a-x \qquad\qquad x \ \text{(in mol./l.)}$$

$$K=x/(a-x)(d-x) \qquad pK=-\log K \qquad (1)$$

The apparent molar extinction coefficient of the complex, ε, can be defined by the following equation:[16]

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[15] The authors wish to express their hearty thanks to Miss Yuriko Matsubayashi of the Government Chemical Industrial Research Institute, Tokyo, for measuring the Raman spectra.

[16] $\varepsilon=(I_T-I_A)/d$, where I_T and I_A are the optical densities of the cyclohexene-silver perchlorate-water system and the aqueous solution of silver perchlorate respectively; they can be represented by the following equations: $I_T=\{x\varepsilon_C+(a-x)\varepsilon_A\}$ (for $\lambda>220$ mμ) and $I_A=a\varepsilon_A$.

$$\varepsilon = x(\varepsilon_C - \varepsilon_A)/d \qquad (2)$$

where ε_C and ε_A are the molar extinction coefficients of the complex and silver perchlorate respectively at a certain wavelength. Setting d as a constant value, ε is dependent on the salt concentration (a), as is shown in Fig. 1, through the unknown parameters K and ε_C. By trial and error calculations, we actually estimated the pK and ε_C values in such a way that the dependence of ε on a can be explained as well as possible. The results are as follows:

$$\mathrm{p}K = 0 \sim -2$$

$$\varepsilon_C = 10^3 \sim 10^4 \quad \text{for} \quad 220 \sim 230\ \mathrm{m}\mu$$

Although the pK value obtained by the present authors is not accurate because of the superposition of the strong absorption of silver perchlorate, it is consistent with the value (p$K = -1.9$) obtained by Winstein and Lucas[3] from distribution experiments.

The Infrared and Raman Spectra of the Complexes. — The infrared absorption spectra of the Nujol and hexachlorobutadiene mulls of the solid complex of (cyclohexene)$_2$-AgClO$_4$[14] are shown in Fig. 2,[17] together with that of pure liquid cyclohexene. The former two spectra are in fairly good agreement with each other in the region where both solvents are transparent. The wave numbers of the observed bands of the complex are tabulated in Table I, compared with those of pure cyclohexene. The olefinic C–H out-of-plane bending band at 716 cm^{-1} shifts to a higher frequency, 748 cm^{-1}, in the complex. It is reported that this type of band in monoölefinic steroids also shifts to higher frequencies with the increasing strain in the ring.[18] The 900 and 1350 cm^{-1} bands intensified by the complex formation are assigned to C–H out-of-plane and in-plane bendings respectively. Although the assignment of the broad and weak 1900 cm^{-1} band has not yet been established, it is interesting to note that the frequency shift of +33 cm^{-1} is the same as that of 900 cm^{-1} band (+32 cm^{-1}). The olefinic C–H stretching band at 3020 cm^{-1} of free cyclohexene is weakend to

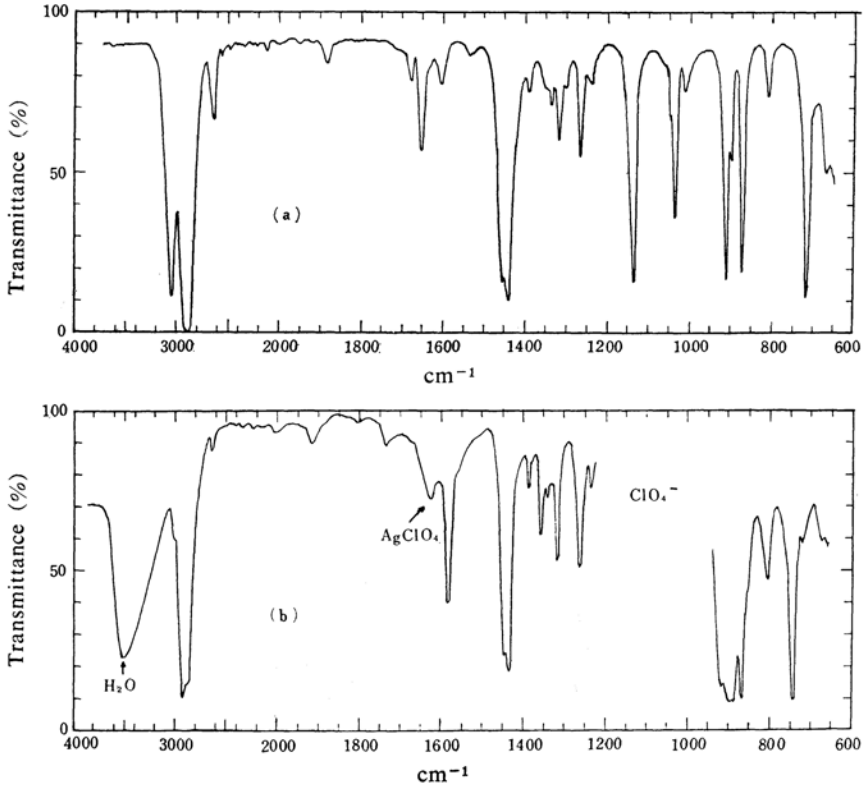

Fig. 2. Infrared absorption spectra of (a) pure cyclohexene and (b) the Nujol and hexachlorobutadiene mulls of the solid complex of $(C_6H_{10})_2 \cdots AgClO_4$.[17]

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[17] The Spectrum of the complex shown in Fig. 2b was synthesized by a complimentary combination of the spectra in Nujol and hexachlorobutadiene mulls. Accordingly, its absolute intensity is somewhat uncertain.

[18] H. B. Henbest, G. D, Meakins and G. W. Wood, *J. Chem. Soc.*, **1954**, 800; H. B. Henbest, G. D. Meakins, B. Nicholls and R. A. L. Wilson, ibid., **1957**, 997.

TABLE I. INFRARED ABSORPTION BANDS (IN cm^{-1}) WITH TENTATIVE ASSIGNMENTS OF PURE C_6H_{10} AND THE SOLID COMPLEX OF $(C_6H_{10})_2 \cdots AgClO_4$

Liquid C_6H_{10}	Solid $(C_6H_{10})_2 \cdots AgClO_4$		
	In Nujol	In HCBD	
3020 (s)		3000 (vw)	C–H Stretching (olef.)
2925 (vs)		2924 (vs)	C–H Stretching
2850 (vs)		2850 (vs)	C–H Stretching
2643 (m)	2645 (w)	2645 (w)	
2560 (vw)	2570b (vw)	2570b (vw)	
2460 (vw)	2460b (vw)	2460 (vw)	
2350b (vw)			
2245 (vw)	2245 (vw)	2245 (vw)	
2195 (vw)		2195b (vw)	
	2130 (vw)	2130 (vw)	
2100 (w)			
	2015 (w)	2015 (w)	
1950b (vw)			
	1914 (w)	1914 (w)	?
1881 (w)			
1790 (vw)	1795 (vw)	1795 (vw)	
1745b (vw)	1738 (w)	1738 (w)	
1709 (vw)			
1680 (w)			
1653 (m)		*	C=C Stretching (free)
	1625 (w)	*(~1625b)	$AgClO_4$
1605 (w)		*	
	1582 (m)	*(~1580b)	C=C Stretching (bonded)
	1560 (vw)		
1530 (vw)			
1446 (s)	*	1448 (s)	
1439 (s)	*	1434 (s)	
1393 (w)	*	1389 (w)	
1351 (vw)	1350 (m)	1350 (m)	C–H In-plane bending
1340 (w)	1338 (w)	1338 (w)	
1322 (m)	1319 (m)	1319 (m)	
1264 (m)	1264 (m)	1264 (m)	
1241 (w)	1238 (w)	1238 (w)	
1215b (vw)	1213 (w)	1213 (w)	
1137 (s)			
1061 (vw)	$\cdots ClO_4^- \cdots$		
1037 (s)			
1008 (w)			
915 (s)	919 (s)	919 (s)	
903 (m)	895b (vs)	895b (vs)	C–H Out-of-plane bending
876 (s)	869 (s)	869 (s)	
808 (m)	808 (m)	*	
	748 (s)	748 (s)	
716 (s)		720b (vw)	C–H Out-of-plane bending
667 (w)	667 (w)	667 (w)	

* Masked by the solvent absorption.

a considerable extent and shifts to a lower frequency, 3000 cm^{-1}, by the complex formation. The band of the complex is so weak that there may be another possibility of its further shift down into the aliphatic C–H stretching frequency region. This fact suggests that the complex formation causes an increase in the strain or a decrease in the s-character in the carbon valence orbital of the C–H bond.

The change in the C=C stretching band is the most prominent. As may be seen in Fig. 3, where the infrared absorption spectra of the complex measured under various conditions are shown, the 1653 cm^{-1} in free cyclohexene is lowered to 1582 cm^{-1} by the complex formation. The result was confirmed by the Raman spectrum measured with the complex under various conditions. This is also consistent with the observation by Taufen et al.[19,20] that the frequency of the ν(C=C) Raman band of cyclohexene is 1575 cm^{-1} in a concentrated silver nitrate solution. The weaker broad peak near 1625 cm^{-1} in the infrared absorption of the complex also appears in the spectrum of the Nujol mull of silver perchlorate and can not be attributed to the absorption of the complex.

All of these changed bands of the complex are pertinent to the C=C double bond part. This probably indicates that the silver ion attacks the C=C bond, weakening its double bond character and giving rise to some strain in the olefinic part. Table II summarizes the observed infrared and Raman bands in 6 and 14 μ regions of cyclohexene under various conditions.[21] It is striking that the perturbed C=C stretching frequencies are almost the same in the solid complex (1582 cm^{-1} for $(C_6H_{10})_2\cdots AgClO_4$) and in the complex in solution (1585 cm^{-1} for $C_6H_{10}\cdots AgClO_4$). This seems to suggest that the complex is in a similar state in a solid and in a solution.

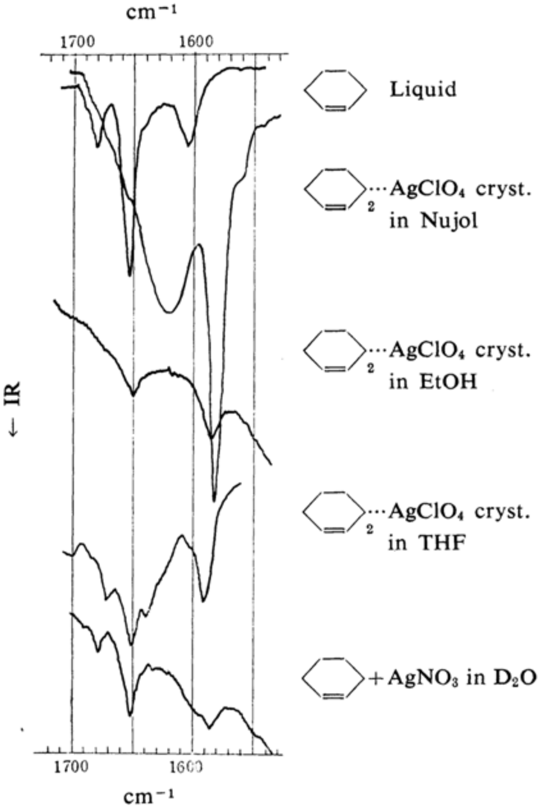

Fig. 3. Infrared absorption spectra of the 6 μ region of cyclohexene under various conditions.

A Theoretical Consideration of the Cyclohexene-Silver Perchlorate Complex

In the present theoretical study, the geometry of the cyclohexene-silver ion complex was assumed to be shown in Fig. 4 by analogy with those of the benzene-silver perchlorate[22a] and cycloöctatetraene-silver nitrate[22b] complexes. The electronic states of the complex were calculated by considering the interaction among the ground configuration and the several excited configurations caused by local excitations within the components and by charge-transfers between them.[23,24]

Component AO's and MO's.—For the olefinic part, besides the 2pπ bonding (φ_1) and 2pπ^* antibonding (φ_2) orbitals, the 3sσ bonding (φ_3) orbital was taken into account. These molecular orbital wave functions can be represented as follows:

$$\varphi_1=(\chi_1{}^{2p}+\chi_2{}^{2p})/\sqrt{2(1-S_{2p\pi})} \qquad (3)$$

$$\varphi_2=(\chi_1{}^{2p}+\chi_2{}^{2p})/\sqrt{2(1-S_{2p\pi})} \qquad (4)$$

$$\varphi_3=(\chi_1{}^{3s}+\chi_2{}^{3s})/\sqrt{2(1+S_{3s})} \qquad (5)$$

Concerning the silver ion, two of the five 4d orbitals, 4d$_{zx}$ (χ_d) and 4d$_{z^2}$ (χ_e) and 5s (χ_s) orbitals were considered,[25] the x, y and z axes being taken as shown in Fig. 4. The component orbitals φ_1, φ_3, χ_e and χ_s are symmetric (S=A$_1$), while φ_2 and χ_d are antisymmetric (A=B$_2$) with respect to the σ_v plane. All the atomic orbitals are of the Slater type.

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[19] H. J. Taufen, M. J. Murray and F. F. Cleveland, *J. Am. Chem. Soc.*, **63**, 3500 (1941).

[20] This is the only spectroscopic result reported hitherto about this type of complex.

[21] All cyclohexene molecules interact with silver perchlorate in the solid complex, while in alcoholic and tetrahydrofuran solutions the complex and the free components are in equilibrium. The cyclohexene-silver nitrate complex is also in equilibrium with free components in (deuterated) water. Contrary to this, Taufen et al.[18] obtained no Raman band of free cyclohexene in its aqueous silver nitrate solution.

[22] a) H. G. Smith and R. E. Rundle, *J. Am. Chem. Soc.*, **72**, 5337 (1950); **80**, 5075 (1958).
b) F. S. Mathews and W. N. Linscomb, *J. Phys. Chem.*, **63**, 845 (1959).

[23] H. C. Longuet-Higgins and J. N. Murrell, *Proc. Phys. Soc.*, **A68**, 601 (1955); J. N. Murrell, ibid., **A68**, 969 (1955); J. A. Pople, ibid., **A68**, 81 (1955).

[24] J. Tanaka, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), **78**, 1636 (1957); **79**, 1373 (1958); S. Nagakura, *Mol. Phys.*, **3**, 105 (1960); H. Hosoya, J. Tanaka and S. Nagakura, This Bulletin, **33**, 850 (1960); H. Hosoya, J. Tanaka and S. Nagakura, *Tetrahedron*, **18**, 859 (1962).

[25] The 4d$_{x^2-y^2}$ orbital with A$_1$ symmetry character is excluded from the calculation, because of its smaller overlap with φ_1 or φ_2 (see Figs. 5 and 6 in Ref. 62). The remaining 4d$_{xy}$ and 4d$_{yz}$ orbitals can not interact with the φ_1, φ_2 and φ_3 MO's of the olefinic part because of their different symmetry properties.

TABLE II. INFRARED AND RAMAN SPECTRA OF 6 AND 14 μ REGIONS OF CYCLOHEXENE UNDER VARIOUS CONDITIONS (IN cm^{-1})

	Added reagent	Solvent[a]	Cell[a]	C=C Stretching				C-H Out-of-plane bending	
				Free			Bonded	Bonded	Free
IR	None	None	NaCl	1680	1653	1605			716
	None	EtOH	NaCl	1682	1653	1606			—[b]
	$Cd(ClO_4)_2$	THF	PE	1680	1652	1600			—
	AgCl	Nujol	NaCl		1650				—
	Ag_2SO_4	Nujol	NaCl	1680	1652	1605			—
	$AgNO_3$	D_2O	PE	1680	1653		1585[c]		—
	$AgNO_3$[g]	Nujol	NaCl				d)		
	$AgClO_4$	EtOH	NaCl		1650[e]		1585[c]		—
	$AgClO_4$	THF	NaCl		1650[e]		1585[c]	740	715
	$AgClO_4$	THF	PE	1680	1650[e]		1585[c]	740	—
	$AgClO_4$[g]	Nujol	NaCl		1625[e]		1582	748	
	$AgClO_4$[g]	HCBD	NaCl		—		1582	748	
	$AgClO_4$[g]	KBr	None				f)		
Raman	None	None	Pyrex		1650				720
	$AgClO_4$	THF	Pyrex		1655[c]		1585[c]		—
	$AgClO_4$	aqMeOH	Pyrex		1665[c]		1575[c]		—
	$AgNO_3$	H_2O[h]	Glass				1584		

a) THF : Tetrahydrofuran, HCBD : Hexachlorobutadiene, PE : Polyethylene
b) The dashed line regions are masked by the absorption of the solvent and/or cell material.
c) $\pm 5\ cm^{-1}$
d) Prevented by water deposited on the cooled cell surface.
e) Band due to solid $AgClO_4$.
f) C_6H_{10} was pumped out from the solid mixture of C_6H_{10}-$AgClO_4$ complex and KBr powder, leaving the yellowish color of AgBr on the disk.
g) Solid complex.
h) Ref. 19

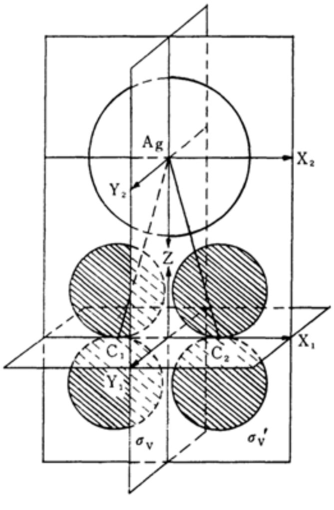

Fig. 4. The geometry of the monoölefin-metal ion complex. For $C_6H_{10}\cdots Ag^+$ the C_1-C_2 and the two Ag-C distances are 1.34 and 2.50Å, respectively.

Configurations and Their Energies.—Five symmetric (ψ_N, ψ_P, ψ_Q, ψ_R and ψ_S) and three antisymmetric (ψ_V, $\psi_{Q'}$ and $\psi_{S'}$) singlet configurations were taken into consideration. These configurations are given in Table III and Fig. 5. Among them, ψ_N, ψ_P and ψ_Q correspond to the no-bond, σ-type charge-transfer and π-type charge-transfer structures[5] respectively. The ψ_S (d-s transition) is the configuration in which one of the 4d orbital electrons of silver ion is excited to the 5s orbital. The importance of ψ_R (corresponding to the Rydberg transition in the olefinic part) has hitherto been overlooked; its inclusion is one of the important characteristics of the present theoretical treatment.[26]

The energy of the no-bond configuration, E_N, being taken as the standard, E_V and E_R can be taken to be equal to the observed transition energies corresponding to the N→V ($\pi \rightarrow \pi^*$ 6.79 eV.) and N→R (Rydberg 5.92 eV.) transitions of cyclohexene respectively.[27] E_S and $E_{S'}$ (5.71 eV.), the so-called singlet d-s separation energy, were obtained from the

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[26] The important role of the $3s\sigma$ bonding orbital in the charge-transfer process will be explained in a coming paper about the mechanism of "trans-addition."

[27] W. J. Potts, Jr., *J. Chem. Phys.*, 23, 65 (1955).

TABLE III. ELECTRONIC CONFIGURATIONS FOR THE $C_6H_{10}\cdots d^{10}$ TYPE METAL ION COMPLEXES

Symmetric	
$\psi_N=(1\bar{1}d\bar{d}e\bar{e})$[a]	
$\psi_P=1/\sqrt{2}\{(1\bar{s}d\bar{d}e\bar{e})+(s\bar{1}d\bar{d}e\bar{e})\}$	Charge-transfer (σ-type)
$\psi_Q=1/\sqrt{2}\{(1\bar{1}d\bar{2}e\bar{e})+(1\bar{1}2\bar{d}e\bar{e})\}$	Back charge-transfer (π-type)
$\psi_R=1/\sqrt{2}\{(1\bar{3}d\bar{d}e\bar{e})+(3\bar{1}d\bar{d}e\bar{e})\}$	Rydberg
$\psi_S=1/\sqrt{2}\{(1\bar{1}d\bar{d}e\bar{s})+(1\bar{1}d\bar{d}s\bar{e})\}$	d-s Transition
Antisymmetric	
$\psi_V=1/\sqrt{2}\{(1\bar{2}d\bar{d}e\bar{e})+(2\bar{1}d\bar{d}e\bar{e})\}$	N → V Transition
$\psi_{Q'}=1/\sqrt{2}\{(1\bar{1}d\bar{d}e\bar{2})+(1\bar{1}d\bar{d}2\bar{e})\}$	Back charge-transfer (π-type)
$\psi_{S'}=1/\sqrt{2}\{(1\bar{1}d\bar{s}e\bar{e})+(1\bar{1}s\bar{d}e\bar{e})\}$	d-s Transition

a) The complete form is expressed as follows:

$$(1\bar{1}d\bar{d}e\bar{e})=\frac{1}{\sqrt{6!}}\sum_{p}(-1)^{p}P\left\{\begin{matrix}\varphi_1(1) & \varphi_1(2) & \chi_d(3) & \chi_d(4) & \chi_e(5) & \chi_e(6)\\ \alpha(1) & \beta(2) & \alpha(3) & \beta(4) & \alpha(5) & \beta(6)\end{matrix}\right\}$$

atomic spectral data collected by Moore.[28] The energies of the three charge-transfer configurations were calculated by means of the following equations:

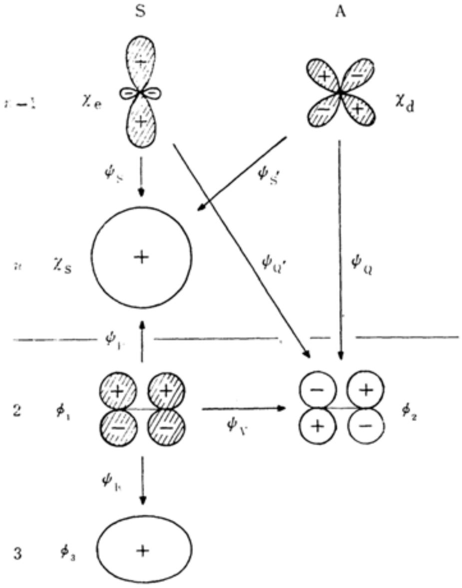

Fig. 5. Schematic representation of the component orbitals and the electron configurations important for the ground and lower excited states of the monoölefin-d^{10} type metal ion complex. These atomic or molecular orbitals are shaded which are doubly occupied in the ground configuration ψ_N. The letters $n-1$ and n for the metal ion and 2 and 3 for the monoölefin indicate the principal quantum numbers of the orbitals in the respective row, while the letters S (symmetric) and A (antisymmetric) represent the symmetry properties, with respect to the σ_v plane, of the orbitals in the respective column. The configurations represented by the vertical arrow have the same symmetry property as the ground configuration does and contribute to lower its energy.

$$E_P=I_{C_6H_{10}}-A_{Ag^+}+0.8\cdot S_{Ag^+}$$
$$=9.00-7.58+4.45=5.87\text{ eV.}$$
$$E_Q=E_{Q'}=I_{Ag^+}-A_{C_6H_{10}}-2e^2/R-0.8\times3/4S_{Ag^+}$$
$$=21.49+0.10-11.52-3.34=6.73\text{ eV.}$$

where the I's and A's are ionization potentials and electron affinities respectively. $A_{C_6H_{10}}$ was assumed to be -0.10 eV. so as to make the sum $I+A=8.90$ eV. for alternant hydrocarbons.[29] S_{Ag^+}, the hydration energy of the silver ion, was calculated by Oshida and Horiguchi.[30] R is the distance between the silver ion and one of the olefinic carbon atoms, 2.50 Å. A detailed description of the derivation of these equations will be given later in this paper.

Configurational Interaction.—The off-diagonal matrix elements of the total electronic Hamiltonian were accounted for only by means of the core resonance integral β.[31] For example:

$$H_{NP}=1/\sqrt{2}\int(1\bar{1}d\bar{d}e\bar{e})\boldsymbol{H}\{(1\bar{s}d\bar{d}e\bar{e})+(s\bar{1}d\bar{d}e\bar{e})\}dv$$
$$=\sqrt{2}\int\varphi_1\boldsymbol{H}^{(1ddee)}\chi_s\,dv=\sqrt{2}\,\beta_{1s}^{(1ddee)}$$

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[28] C. E. Moore, "Atomic Energy Levels," Vols. I, II, III, National Bureau of Standards (1949, 1952, 1958).

[29] N. S. Hush and J. A. Pople, *Trans. Faraday Soc.*, **51**, 600 (1955).

[30] I. Oshida and D. Horiguchi, *Bull. Kobayashi Inst. Phys. Res.*, 5, 61 (1955) (in Japanese); *J. Phys. Soc. Japan*, **11**, 330 (1956).

[31] Generally speaking, the off-diagonal matrix elements comprise non-zero terms due to two-center Coulomb repulsion integrals. For example, $H_{RS}=(13\mid se)=\int\varphi_1{}^*(1)\times\varphi_3(1)(e^2/r_{12})\chi_e{}^*(2)\chi_s(2)dv$ contains non-zero Coulomb repulsion integral terms. However, this can be disregarded, as is clear from the following consideration. H_{RS} can be represented approximately by $\boldsymbol{\mu}_{13}\cdot\boldsymbol{\mu}_{es}/R$, where $\boldsymbol{\mu}_{13}=e\int\varphi_1\boldsymbol{r}\varphi_3dv$ and $\boldsymbol{\mu}_{es}=e\int\chi_e\boldsymbol{r}\chi_s dv$. The latter quantity is zero because it corresponds to the transition moment between s and d orbitals within the silver atom. The $H_{VS'}=(12\mid ds)$ value can also be disregarded.

TABLE IV. EFFECTIVE CHARGES AND IONIZATION ENERGIES OF ELECTRONS FOR VARIOUS STATES OF CYCLOHEXENE OBTAINED FROM SPECTROSCOPIC RESULTS

Electronic configuration[a]	Ionizing electron	Slater's μ factor[38]	Ionization energy, eV.	Remark[b]
(11)	1	1.625	9.00	$=I_{C=C}$
(112)	2	1.45	−0.10	$=A_{C=C}$
(12)	2	1.625	2.21	$=I_{C=C}-\Delta E_{N\to V}$
(13)	3	0.483	3.08	$=I_{C=C}-\Delta E_{N\to R}$
(112)	1	1.45	6.69	$=\Delta E_{N\to V}+A_{C=O}$

a) 1, 2 and 3 are the molecular orbitals φ_1, φ_2 and φ_3, respectively.
b) I: Ionization potential;[33,34] A: Electron affinity (assumed); ΔE: Transition energy[27]

where $\beta_{1s}^{(1ddee)}$ is the core resonance integral between the φ_1 and χ_s orbitals in the core potential field of $\boldsymbol{H}^{(1ddee)}$, which is the common part in the two configurations, ψ_N and ψ_P. According to Mulliken,[32] this value is approximated as proportional to the product of the overlap integral, $S_{1s}^{(1ddee)}$, and the mean ionization potential, $\bar{I}$.

$$\beta_{1s}^{(1ddee)}=C\cdot S_{1s}^{(1ddee)}\cdot\bar{I}$$
$$=C\cdot S_{1s}^{(1ddee)}\{I(11\to 1)+I(ddees\to ddee)\}/2 \qquad (6)$$

Here C is a constant, and $I(11\to 1)$ and $I(ddees\to ddee)$ are the ionization potentials of cyclohexene and of the silver atom respectively.

The first ionization potential of cyclohexene was determined to be 9.00 eV. from the data of Watanabe[33] and others.[34] The values of the ionization energies for the other states of cyclohexene were estimated by combining the first ionization potential value with the spectroscopic data (see Appendix I). These values are summarized in Table IV, while the values for the metal ion part were taken from Moore's table.[28] The overlap integrals were mostly calculated from the published tables[35-37] but partly, where necessary, from our new tables (see Appendix II) by assuming appropriate effective charges for the Slater-type AO's.[38] The formulae for the iterative degradation of overlap integrals between the various types of d-orbitals and the olefinic p-orbitals into simpler forms are listed in Appendix III. The proportional constant, C, was evaluated to be -1.0,[39] by taking into account the following relation for ethylene:

$$\beta=C\cdot S\cdot I_C=-3.125$$
$$=-1.003\times 0.270\times 11.54 \text{ (eV.)}$$

where β is the value adopted by Pariser and Parr[41] and I_C, the $2p\pi$ valence state ionization potential of a carbon atom.[42] The non-zero off-diagonal elements thus obtained are included in Table IX.

The Stabilization Energy and the CT-R Band of the Cyclohexene-Silver Perchlorate Complex.—The secular equations constructed from the matrix elements evaluated as mentioned above were solved by the aid of an IBM 7090 electronic computer. Among the evaluated energy levels and wave functions, those for the lowest three levels are tabulated in Table V (see also Fig. 6).

According to the present theoretical study, the complex is stabilized by charge-delocalization by about 1.05 eV., with the 7.4 and 6.9 per cent contributions of the ψ_P and ψ_Q charge-transfer configurations respectively. The Rydberg configuration contributes to the ground state by 2.0 per cent. The in-phase mixing of the widely extended $3s\sigma$ orbital with the $2p\pi$ bonding orbital corresponds to the polarization of the latter electronic cloud toward the silver ion, especially in the outer skirts.

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32) R. S. Mulliken, *J. Phys. Chem.*, **56**, 295 (1952).

33) K. Watanabe, *J. Chem. Phys.*, **26**, 542 (1957).

34) W. C. Price and W. T. Tutte, *Proc, Roy. Soc.*, **A174**, 207 (1940); J. D. Morrison, *J. Chem. Phys.*, **19**, 1305 (1951); J. Hissel, *Bull. Soc. Roy. Sci. Liège*, **21**, 457 (1952).

35) R. S. Mulliken, C. A. Rieke, D. Orloff and H. Orloff, *J. Chem. Phys.*, **17**, 1248 (1949).

36) D. P. Craig, A. Maccoll, R. S. Nyholm, L. E. Orgel and L. E. Sutton, *J. Chem. Soc.*, **1954**, 332,

37) H. H. Jaffé and G. O. Doak, *J. Chem. Phys.*, **21**, 196 (1953); H. H. Jaffé, ibid., **21**, 258 (1953); J. L. Roberts and H. H. Jaffé, ibid., **27**, 883 (1957).

38) J. C. Slater, *Phys. Rev.*, **36**, 57 (1930).

39) If Eq. 6 be taken as proven, two problems still remain. One is whether the use of Slater-type wave functions for the silver 4d and 5s orbitals gives correct values for the overlap integrals, S's, which in principle should be calculated with the SCF orbitals. According to the test calculation by Mulliken et al.,[35] there arose no serious dircrepancy between the $S(2p\sigma C, 2p\sigma C)$ values calculated with Slater-type and SCF functions, especially for the bond length region around 2 Å (the S(SCF)/S(Slater) ratio being 1.4~0.7). By the use of numerical tables for metal s-orbitals calculated by Hartree et al.[40] with the SCF method, the $S(2p\sigma C$(Slarer), $4sZn^+$(SCF); 2.06 Å) value was numerically calculated and compared with the $S(2p\sigma C$(Slater), $4sZn^+$(Slater); 2.06 Å) value. The agreement was found unexpectedly well (the ratio being 1.2= 0.21/0.17).

The other is whether the semi-empirical parameter, C, is applicable to the intermolecular lateral overlaps. In the present study, we have made calculations for the three cases of $C=-0.6$, -0.8 and -1.0.

40) W. Hartree, D. R. Hartree and M. F. Manning, *Phys. Rev.*, **59**, 299 (1940).

41) R. Pariser and R. G. Parr, *J. Chem. Phys.*, **21**, 466, 767 (1953).

42) H. O. Pritchard and H. A. Skinner, *Chem. Revs.*, **55**, 745 (1955).

TABLE V. WAVE FUNCTIONS AND ENERGIES OF THE LOWER ELECTRONIC STATES OF THE $C_6H_{10}\cdots Ag^+$ COMPLEX

$W_0=-1.052$ eV. $\Psi_0=\ \ 0.9125\phi_N+0.2717\phi_P+0.2624\phi_Q+0.1416\phi_R-0.0676\phi_S$
$W_1=\ \ 2.150$ $\Psi_1=-0.2745\phi_N+0.6489\phi_P-0.1341\phi_Q+0.6257\phi_R-0.3068\phi_S$
$W_2=\ \ 4.487$ $\Psi_2=\ \ 0.7024\phi_V-0.7117\phi_{Q'}$
$W_3=\ \ 5.710$ $\Psi_3=\phi_{S'}$
$W_4=\ \ 5.747$ $\Psi_4=-0.0025\phi_N+0.0200\phi_P-0.0058\phi_Q+0.4214\phi_R+0.9066\phi_S$

TABLE VI. ENERGY LEVELS OF THE GROUND AND LOWEST EXCITED STATES OF THE $C_6H_{10}\cdots Ag^+$ COMPLEX WITH THEIR PER CENT CONTRIBUTION BY THE SEVERAL CONFIGURATIONS WITH VARYING PARAMETER C

C	$\Delta E=-W_0$ eV.	W_1-W_0 eV.	W_2-W_1 eV.	Ground state				CT-R state			
				ϕ_N	ϕ_P	ϕ_Q	ϕ_R	ϕ_N	ϕ_P	ϕ_Q	ϕ_R
−0.6	0.381	3.933	1.844	94.1	2.2	3.4	0.3	1.9	47.3	40.1	10.4
−0.8	0.675	3.507	2.110	89.4	4.3	5.2	0.8	4.1	45.1	40.0	9.9
−1.0	1.052	3.202	2.337	83.3	7.4	6.9	2.0	7.5	42.1	39.2	9.4

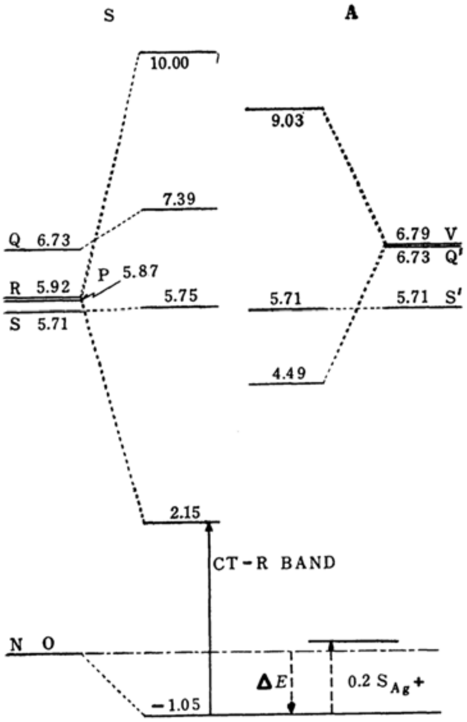

Fig. 6. Energy diagram (in eV.) for the $C_6H_{10}\cdots Ag^+$ complex in water showing configuration interaction, stabilization (ΔE) and destabilization ($0.2\cdot S_{Ag^+}$), and CT–R transition.

The stabilization energy of 1.05 eV. should not be taken literally, since the silver ion is destabilized by the replacement of a portion of the hydrated water molecules by a nonpolar olefin molecule. This energy may be estimated to be about two-tenths of the hydration energy of a silver ion, because the solid angle spanning the cyclohexene molecule from the silver ion in this geometry is just two-tenths of the whole angle. Since the hydration energy of the silver ion is 5.56 eV.,[30] the destabilization energy due to the destruction of the water sheath may be estimated to be 1.11 eV. This is consistent with the electrostatic calculation by Eley and Evans[43] that the enegy requirement for removing one water molecule from the hydration sphere of the silver ion is larger than 20 kcal./mol. (=0.87 eV.). The most important point in the present treatment is that the olefinic π-electron stabilization energy (1.05 eV. = 24.2 kcal./mol.) is comparable to the lost hydration energy (1.11 eV. = 25.6 kcal./mol.).

The lowest excited state, with 42 and 39 per cent contributions by the ϕ_P and ϕ_R configurations respectively, is only 3.2 eV. higher than the ground state. The poor agreement between the observed (∼5.4 eV.) and calculated (∼3.2 eV.) values may possibly be attributed to the use of the macroscopic hydration energy (see later) obtained from the Born-Haber cycle instead of the structure-dependent microscopic hydration energy, and to the lack of detailed quantitative knowledge about the electronic states of larger atoms with d-electrons and intermolecular interaction energies. However, as is evident in Table VI, for calculation with C values varying from −0.6 to −1.0, the lowest excited state is invariably 2 eV. lower than the next higher excited state (V state) and its character is invariant. Namely, ϕ_P and ϕ_R contribute to the lowest excited state by almost the same amount, 40 per cent. The new band at about 230 mμ for the cyclohexene-silver ion complex is, then, determined to have the mixing character of charge-transfer from the olefin to the silver ion and the Rydberg transition in the olefin part (CT–R band).

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[43] D. D. Eley and M. G. Evans, *Trans. Faraday Soc.*, **34**, 1093 (1938).

A Theoretical Consideration of the Selective-Complex Formation Abilities of Copper(I), Silver(I) and Mercury(II) Ions[44]

In order to clarify the reason why some of the closed shell (d^{10} and p^6)-type metal ions form stable complexes with olefins, while the others can not, we undertook to calculate the stabilization energy due to the electron delocalization for the systems containing various metal ions and cyclohexene, assuming reasonable geometrical configurations. A hypothetical monoölefin-metal ion complex is assumed to have the C_{2v} symmetry property (for the π-electronic part), with R_{MC} equal to $r_{M^{n+}}+1.32$ Å, where 1.32 Å is a constant determined in such a way that R_{MC} for the case of silver ions is equal to 2.50 Å.[51] The ionic and metallic raddii of silver ions are 1.18 and 1.34 Å, while the covalent radius of carbon atoms and the half thickness of aromatic molecules proposed by Pauling[52] are 0.77 and 1.70 Å respectively. That the sum of the respective mean values is equal to 2.50 Å is indeed a fortuitous coincidence, but it may be the ground for some possible additivity relationship.

Since the energy evaluations of the charge-transfer configurations are important in discussing the stabilities of various monoölefin-metal ion complexes, first of all a detailed description will be given of the evaluation of the charge-transfer configurational energy.

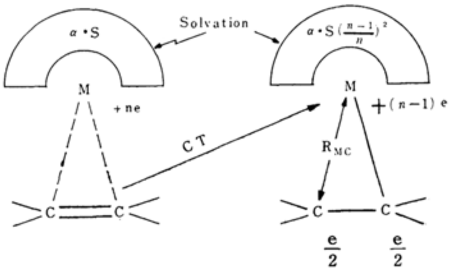
The Estimation of Charge-Transfer Configuration Energies. — The hydration energy of the metal ion may be thought to diminish greatly in the charge-transfer configuration compared with that of the ground configuration. Therefore, in the evaluation of the charge-transfer configuration energy, we must reasonably estimate the magnitude of the change of hydration energy. The solvation energy of a metal ion is known to be roughly proportional to the square of the charge number. If the solvated molecules are assumed not to change their positions during an electron transfer in the solvated cage, the decrease in solvation energy is approximately equal to

$$\alpha\,[n^2-(n-1)^2]/n^2\cdot S_{M^{n+}}=\alpha\,(2n-1)/n^2\cdot S_{M^{n+}}$$

where $S_{M^{n+}}$ is the solvation energy of a metal ion, M^{n+}, and α is a universal parameter representative of effective solvation by the olefin molecules. The energy necessary for an electron transfer from the olefin to the ion may then be estimated as follows:

$$H_{PP}=I_{C=C}-I_{M^{(n-1)+}}+(n-1)e^2/R_{MC}+\alpha\cdot S_{M^{n+}}\cdot(2n-1)/n^2 \qquad (7)$$

where $I_{C=C}$ and $I_{M^{(n-1)+}}$ indicate the ionization potentials of the olefin and the metal ion (or atom) $M^{(n-1)+}$, the latter quantity being identical to the electron affinity of the ion M^{n+}. The third term is the repulsion energy between charges of the metal and carbon atoms (see Fig. 7). In the above treatment, the change in the solvation energy of the olefinic part is disregarded, since the resulting net charge is divided into two carbon atoms and since, moreover, they are shielded by the other carbon and hydrogen atoms to a considerable extent. Even if it can not completely be disregarded, it may conceivably be included in the unknown parameter, α, the determination of which is the next problem.



$$I_{C=C}-I_{M^{(n-1)+}}+\frac{(n-1)\cdot e^2}{R_{MC}}+\frac{\alpha\cdot \boldsymbol{S}\cdot(2n-1)}{n^2}$$

Fig. 7. Estimation of the charge-transfer configurational energy H_{PP}.

We have plotted the $(2n-1)\cdot S_{M^{n+}}/n^2$ $(=X)$ values for twenty-five d^{10} and p^6-type metal ions and for the halogen cations Br^+ and I^+ against the sum (Y) of the first three terms in Eq. 7 by using the following values: $I_{C=C}=9.00$ eV. for cyclohexene;[33] $I_{M^{(n-1)+}}$, from Moore's table;[28] $R_{MC}=1.32+r_{M^{n+}}$ Å, where the $r_{M^{n+}}$'s were taken from the table of ionic radii by Stockar;[53] the $S_{M^{n+}}$ value was taken from the table of hydration energies by Oshida and Horiguchi[30] (see Table VII). It may easily be shown that, for a fixed α value, the points for the metal ions with the same charge-transfer

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44) The complexes considered here differ from such square planar Zeise salts as $K[(C_2H_4)\cdot PtCl_3]$[45], such transition metal carbonyl-olefin complexes as $C_5H_8\cdot Fe(CO)_3$[46] or such mercury ion-olefin addition compounds as $HO\cdot CH_2CH_2\cdot HgCl$,[47] which are shown to have true or nearly covalent metal-carbon bonds by the evidence of X-rays,[48] infrared absorption,[49] NMR spectroscopy[50] and from some other chemical properties.

45) W. C. Zeise, *Pogg. Ann.*, **9**, 632 (1827).

46) M. A. Benett, *Chem. Revs.*, **62**, 611 (1962).

47) J. Chatt, ibid., **48**, 7 (1951).

48) P. R. H. Alderman, P. G. Owston and J. M. Rowe, *Acta Cryst.*, **13**, 149 (1960).

49) J. Chatt and L. A. Duncanson, *J. Chem. Soc.*, **1953**, 2939; J. Chatt and M. L. Searle, "Inorganic Syntheses," 5, Ed. by Moeller., McGraw-Hill, New York (1957), p. 210.

50) D. B. Powell and N. Sehenert, *J. Chem. Soc.*, **1960**, 2519.

51) R_{MC} and $r_{M^{n+}}$ are, respectively, the carbon-metal distance and the ionic radius of a metal ion, M^{n+}.

52) L. Pauling, "The Nature of the Chemical Bond," Cornell Univ. Press, Ithaca, New York (1960).

53) K. Stockar, *Helv. Chim. Acta*, **33**, 1409 (1950).

TABLE VII. EVALUATION OF H_{PP} VALUES

Ion	Lewest vacant orbital	$I_{M^{(n-1)+}}$ Å	$r_{M^{n+}}$ Å	$\boldsymbol{S}_{M^{n+}}$ eV.	Y[b] eV.	X[a] eV.	$Y+0.8X=H_{PP}$ eV.
Na^+	3s	5.14	0.86	4.61	3.86	4.61	6.55
K^+	4s	4.34	1.22	3.75	4.66	3.75	7.67
Rb^+	5s	4.18	1.40	3.52	4.82	3.52	7.63
Cs^+	6s	3.89	1.61	3.19	5.11	3.19	7.66
Mg^{2+}	3s	15.03	0.65	20.61	1.28	15.46	13.65
Ca^{2+}	4s	11.87	0.99	17.04	3.36	12.78	13.59
Sr^{2+}	5s	11.03	1.15	15.69	3.80	11.77	13.22
Ba^{2+}	6s	10.00	1.37	14.81	4.35	11.11	13.24
Al^{3+}	3s	28.45	0.61	49.46	− 4.53	27.48	17.46
Sc^{3+}	3d	24.76	0.81	43.51	− 2.24	24.17	17.10[c]
Y^{3+}	4d	20.55	0.95	38.82	1.14	21.57	18.40[c]
Ti^{4+}	3d	43.25	0.68	84.69	−12.65	37.05	17.00[c]
Zr^{4+}	4d	34.34	0.80	70.85	− 4.96	31.00	19.84[c]
Cu^+	4s	7.73	0.90	6.47	1.27	6.47	6.45
Ag^+	5s	7.58	1.18	5.56	1.42	5.56	5.87
Au^+	6s	9.23	1.29	6.81	− 0.23	6.81	5.22
Zn^{2+}	4s	17.96	0.74	21.90	− 1.97	16.43	11.17
Cd^{2+}	5s	16.91	0.97	19.41	− 1.62	14.56	10.03
Hg^{2+}	6s	18.76	1.10	19.51	− 3.81	14.63	7.89
Ga^{3+}	4s	30.71	0.62	49.20	− 6.86	27.33	15.00
In^{3+}	5s	28.03	0.81	43.99	− 5.51	24.44	14.04
Tl^{3+}	6s	29.83	0.95	44.34	− 8.14	24.63	11.56
Ge^{4+}	4s	45.71	0.54	91.68	−13.48	40.11	18.61
Sn^{4+}	5s	40.73	0.70	89.28	−10.34	39.06	20.91
Pb^{4+}	6s	42.32	0.84	75.88	−13.32	33.20	13.24
Br^+	4p	11.84	0.71	6±1	− 2.84	6±1	2.0±0.8
I^+	5p	10.46	1.05	5±1	− 1.46	5±1	2.5±0.8

a) $X=\boldsymbol{S}_{M^{(n-1)+}}\cdot(2n-1)/n^2$ (eV.)

b) $Y=9.00-I_{M^{(n-1)+}}+(n-1)\cdot e^2/R_{MC}$ (eV.), $R_{MC}=1.32+r_{M^{n+}}$ (Å)

c) These values are $H_{P''P''}$'s, since $H_{P''P''}$ is smaller than H_{PP} for these ions.

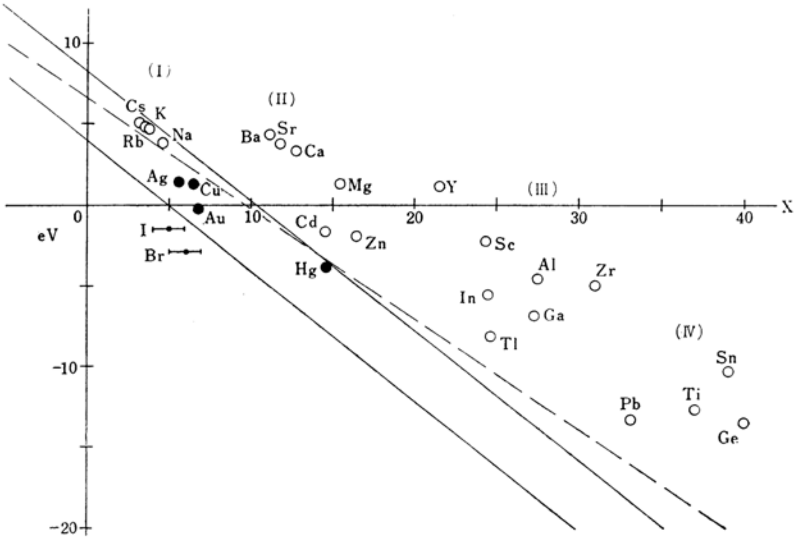

Fig. 8. Determination of α. The two parallel lines have α equal to 0.8, while the broken line 0.7. The Roman numerals indicate the charge numbers of the ions. The ions are classified into three groups:

○ without an ability of complex formation,
● with an ability of complex formation, and
⊢•⊣ with a tendency for further addition reaction.

energy, $H_{PP}=Y+\alpha\cdot X$, lie exactly on a straight line with the slope $-\alpha$ and intercepting the Y axis at $Y=H_{PP}$. The Cu^+, Ag^+, Au^+ and Hg^{2+} ions, together with alkali metal ions, were found distinguishable from the others, since the points for the former ions lie beneath the line with α equal to about 0.8; this indicates that the former ions have lower H_{PP} values than the latter do. In spite of their higher electron affinities the trivalent and tetravalent ions show larger H_{PP} values. This is because the third and fourth terms of Eq. 7, namely, the electrostatic repulsion and solvation energy terms, become larger for these ions and compensate for the smaller value of the $I_{C=C}-I_{M^{(n-1)+}}$ term.

It is interesting to note that the plots for Br^+ and I^+ ions lie in the region for beneath the line, indicating their low H_{PP} values and, accordingly, the possibility of further addition reaction.

Similarly, the energies for the back charge-transfer H_{QQ}'s for twelve d^{10}-type metal ions were evaluated by the following equation:

$$H_{QQ}=I_{M^{n+}}-A_{C=C}-(n+1)e^2/R_{MC}-0.8\cdot S_{M^{n+}}(2n+1)/(n+1)^2 \qquad (8)^{54)}$$

where $A_{C=C}$ is the electron affinity of cyclohexene, -0.10 eV. (estimated). Again, Cu^+, Ag^+, Au^+ and Hg^{2+} have much lower H_{QQ} values than do any other metal ions (see Table VIII). This fact is also closely related to the selected abilities of Cu^+, Ag^+ and Hg^{2+} for complex formation with monoölefins.

TABLE VIII. EVALUATION OF H_{QQ} VALUES

Ion	Highest occupied orbital	$I_{M^{n+}}$ eV.	X a) eV.	Y b) eV.	$H_{QQ}=Y+0.8X$ eV.
Cu^+	3d	20.29	4.85	7.42	3.54
Ag^+	4d	21.49	4.17	10.07	6.73
Au^+	5d	20.50	5.11	9.57	5.48
Zn^{2+}	3d	39.71	12.17	18.84	9.10
Cd^{2+}	4d	37.48	10.78	18.72	10.10
Hg^{2+}	5d	34.20	10.84	16.45	7.78
Ga^{3+}	3d	64.17	21.53	34.58	17.36
In^{3+}	4d	54.40	19.25	27.46	12.06
Tl^{3+}	5d	50.72	19.40	25.45	9.93
Ge^{4+}	3d	93.45	33.00	54.84	28.44
Sn^{4+}	4d	72.30	32.14	36.76	11.05
Pb^{4+}	5d	68.80	27.32	35.57	13.71

a) $X=S_{M^{n+}}\cdot(2n+1)/(n+1)^2$ (eV.)

b) $Y=I_{M^{n+}}+0.10-(n+1)\cdot e^2/R_{MC}$ (eV.)
$R_{MC}=1.32+r_{M^{n+}}$ (Å)

The Estimation of Stabilization Energies for Various Monoölefin-Metal Ion Complexes.—The stabilization energies were estimated on the basis of charge-transfer configurational energies evaluated by the above-mentioned method.

The component MO's and AO's are the same as those for the silver complex. The effective charges and orbital energies were determined according to the Slater rule,[38] and by the atom ionization potentials and atomic spectral data,[28] respectively.

In this calculation, only the singlet symmetric (with respect to the yz plane), $^1A_1$, configurations are considered, because we are concerned with rough estimations of stabilization energies due to charge delocalization and of the loss in hydration energies. The H_{PP}'s for the d^{10}- and p^6-groups and the H_{QQ}'s for the d^{10}-group were estimated by the method described in the preceding section. H_{RR} is again 5.92 eV. Since, for the p^6-group ions, the energy separations between the ns- and np-orbitals are generally small (a few eV.), another charge-transfer configuration, $\psi_{P'}$ namely, the one caused by the charge-transfer from φ_1 to χ_{npz} (χ_p) was considered. For Sc^{3+}, Y^{3+}, Ti^{4+} and Zr^{4+}, with $(n-1)$d but not ns-orbital as the lowest vacant one, an extra charge-transfer configuration, $\psi_{P''}$, namely, the one caused by the charge-transfer from φ_1 to $\chi_{(n-1)dz^2}$ ($\chi_{e'}$; see Fig. 9) was considered. These configurational energies, $H_{P'P'}$ and $H_{P''P''}$'s, were determined by the algebraic addition of the doublet p-s $((n-1)p^6\cdot ns\rightarrow(n-1)p^6\cdot np)$ and d-s $((n-1)p^6\cdot ns\rightarrow(n-1)p^6\cdot(n-1)d)$ separation energies of $M^{(n-1)+}$ ion (or atom) to the H_{PP} values. The H_{SS}'s for the

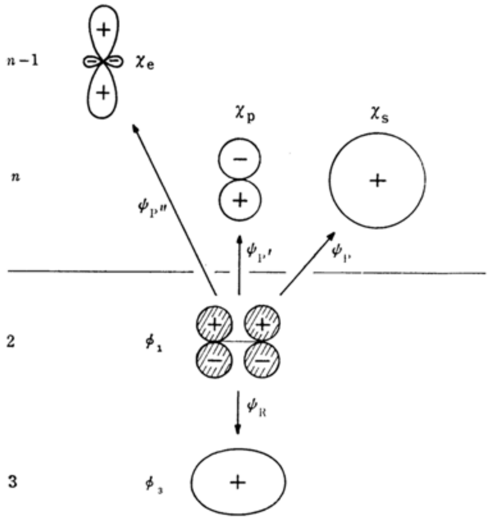

Fig. 9. Schematic representation of the component orbitals and the electron configurations (symmetric) of the hypothetical monoölefin-p^6 type metal ion complex. See the caption of Fig. 5.

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[54] The choice of $(2n+1)/n^2$ instead of $(2n+1)/(n+1)^2$ for the coefficient of $0.8\cdot S_{M^{n+}}$ in the last term was proved to give abnormally lower energies for H_{QQ}.

TABLE IX. NON-ZERO MATRIX ELEMENTS (IN eV.) FOR THE $C_6H_{10}\cdots d^{10}$ TYPE METAL ION COMPLEXES

	H_{PP}	H_{QQ}	H_{RR}	H_{SS}	H_{NP}	H_{NQ}	H_{PR}	H_{PS}
Cu^+	6.45	3.54	5.92	3.26	−1.774	−1.385	−3.384	0.900
Ag^+ [a]	5.87	6.73	5.92	5.71	−1.372	−2.238	−3.635	1.683
Au^+	5.22	5.48	5.92	3.67	−1.173	−2.279	−4.302	1.894
Zn^{2+}	11.17	9.10	5.92	10.35	−4.461	−2.605	−5.334	1.474
Cd^{2+}	10.03	10.10	5.92	11.02	−3.334	−4.150	−5.597	2.622
Hg^{2+}	7.89	7.78	5.92	7.57	−3.082	−4.123	−6.705	2.950
Ga^{3+}	15.00	17.36	5.92	19.32	−8.368	−3.851	−7.214	1.948
In^{3+}	14.04	12.06	5.92	17.20	−6.703	−5.951	−7.498	3.606
Tl^{3+}	11.56	9.93	5.92	11.99	−5.986	−6.192	−8.524	3.888
Ge^{4+}	18.61	28.44	5.92	30.00	−13.192	−13.192	−9.221	2.330
Sn^{4+}	20.91	11.05	5.92	23.96	−10.584	−7.301	−9.375	4.311
Pb^{4+}	13.24	13.71	5.92	16.86	−9.870	−7.335	−10.056	4.773

a) $H_{VQ'}=2.273$ eV. for another secular equation concerning the antisymmetric configurations, ψ_V, $\psi_{Q'}$ and $\psi_{S'}$, with respect to the yz (σ_V) plane.

TABLE X. NON-ZERO MATRIX ELEMENTS (IN eV.) FOR THE $C_6H_{10}\cdots p^6$ TYPE METAL ION COMPLEXES

	H_{PP}	$H_{P'P'}$	$H_{P''P''}$	H_{RR}	H_{NP}	$H_{NP'}$	$H_{NP''}$	H_{RP}	$H_{RP'}$	$H_{RP''}$
Na^+	6.55	8.65		5.92	−1.087	−1.021		−3.045	−0.969	
K^+	7.67	9.28		5.92	−0.227	−0.023		−3.095	−1.041	
Rb^+	7.63	9.19		5.92	0.034	0.217		−3.012	−1.210	
Cs^+	7.66	9.05		5.92	0.568	0.255		−2.959	−1.330	
Mg^{2+}	13.65	18.07		5.92	−4.071	−3.066		−4.793	−0.398	
Ca^{2+}	13.59	16.71		5.92	−1.631	−1.284		−5.343	−1.198	
Sr^{2+}	13.22	16.16		5.92	−1.061	−0.799		−5.483	−1.518	
Ba^{2+}	13.24	15.75		5.92	−0.849	−0.746		−5.142	−1.720	
Al^{3+}	17.46	24.06		5.92	−8.320	−6.804		−6.525	−0.153	
Sc^{3+}	20.27	24.80	17.10	5.92	−4.186	−3.520	−4.372	−6.901	−1.021	0.372
Y^{3+}	19.33	23.53	18.40	5.92	−2.979	−2.560	−1.430	−7.057	−1.453	0.099
Ti^{4+}	26.97	32.86	17.00	5.92	−7.740	−6.013	−9.525	−8.421	−0.552	0.683
Zr^{4+}	24.58	30.00	19.84	5.92	−6.116	−5.461	−4.732	−8.439	−0.994	0.395

d^{10} group were determined as the singlet d-s separation energies ($d^{10}\rightarrow d^9\cdot s$) of M^{n+} ions. The offdiagonal elements were calculated in a manner similar to that used for a silver complex ($C=-1.0$). The non-zero matrix elements thus obtained for many metal ion complexes are tabulated in Tables IX and X. By solving the secular equations constructed from the matrix elements for each metal ion complex, the stabilization energy due to charge delocaliztion, ΔE, was evaluated. The results are shown in Table XI.

A Comparison of the Delocalization Energies Evaluated for Various Metal Ion Complexes.— In Table XI the $|\Delta E|$ values are compared with the $0.2\cdot S_{M^{n+}}$ values corresponding to the loss of hydration energy. As is evident from these results, the copper(I), silver(I), gold(I) and mercury(II) ions are distinguished from other closed shell-type metal ions with very small values of $(0.2\cdot S_{M^{n+}}-|\Delta E|)/0.2\cdot S_{M^{n+}}$ and are correlated with the very selective complex formation abilities except for the case of the gold(I) ion. The reason why the stable monoölefin-Au^+ complex can not exist may be due to the infrequent occurrence of the monovalent ion itself.

The fact that ψ_P and ψ_Q contribute to the ground state of copper(I), silver(I) and mercury(II) complexes by almost the same amounts seems to show the importance of the π-type back charge-transfer mechanism.[5] This may be supported by the fact that the p^6 group metal ions without outer d-electrons can not form stable complexes with monoölefins. The overlap integrals between the olefinic carbon, 2pz AO, and χ_s and χ_d have been shown not to deviate substantially from ion to ion, while the energies of the two charge-transfer configurations seem to correlate well with the complex formaton ability. It is interesting to note that a good correlation is also found with the smaller d-s separation energy (H_{SS}) for copper(I), silver(I) and mercury(II) ions

TABLE XI. DELOCALIZATION AND DESTABILIZATION ENERGIES OF THE HYPOTHETICAL COMPLEXES OF THE $C_6H_{10}\cdots$CLOSED SHELL TYPE METAL IONS

Ion	Delocalization energy $\lvert\Delta E\rvert$ eV.	Destabilization energy $0.2\cdot S_{M^{n+}}$ eV.	$\dfrac{0.2\cdot S_{M^{n+}}-\lvert\Delta E\rvert}{0.2\cdot S_{M^{n+}}}$
Na^+	0.36	0.92	0.61
K^+	0.01	0.75	0.99
Rb^+	0.01	0.70	0.99
Cs^+	0.06	0.64	0.91
Mg^{2+}	1.82	4.12	0.56
Ca^{2+}	0.41	3.41	0.88
Sr^{2+}	0.19	3.14	0.94
Ba^{2+}	0.13	2.96	0.96
Al^{3+}	5.26	9.89	0.47
Sc^{3+}	2.48	8.70	0.71
Y^{3+}	1.11	7.76	0.86
Ti^{4+}	6.79	16.94	0.60
Zr^{4+}	3.68	14.17	0.74
Cu^+	0.99	1.29	0.23
Ag^+	1.05	1.11	0.05
Au^+	1.22	1.36	0.10
Zn^{2+}	2.54	4.38	0.42
Cd^{2+}	2.65	3.88	0.32
Hg^{2+}	3.27	3.90	0.16
Ga^{3+}	5.21	9.84	0.47
In^{3+}	5.30	8.80	0.40
Tl^{3+}	5.87	8.87	0.34
Ge^{4+}	8.79	18.34	0.52
Sn^{4+}	7.92	17.86	0.56
Pb^{4+}	9.03	15.18	0.41

(see Table IX). As Orgel[55] has pointed out, the mixing of χ_{dz^2} orbital with a χ_s orbital facilitates the extension of the diagonal valency character.[56] The difficulty polyvalent ions have in forming complexes with olefins can be explained as follows. The destabilization energies ($0.2\cdot S_{M^{n+}}$) of metal ions in the same periodic row are proportional to the square of the charge number (n), whereas the competing delocalization energies (ΔE) were found to be roughly proportional to the three-halves order of the charge number (see Table XI). The reason why, among the divalent ions, mercury(II) ion alone has a selective complex formation ability is not attributed to the difference in its hydration energies or ionic radii but to the instability of its d^{10} state and, hence, its large electron affinity relative to other ions.

Although our calculations appear to be based on some bold assumptions and on arbitrarily numerical parameters, the results obtained here, specifically for the importance of the $3s\sigma$ orbital in the lowest excited state and for the selective complex-formation abilities of copper(I), silver(I) and mercury(II) ions, are invariant. Since both the method of the "composite molecule" and the concepts of charge-transfer and hybridization can be derived as consequeces of a mathematical development describing a true state in terms of quantities with clearer physical meanings, another approach, e. g., the LCAO MO method, to this problem would give similar results.

The Effect of Olefins and Negative Ions upon the Stability of Monoölefin-Metal Ion Complexes. — A similar calculation was made for the ethylene-silver ion complex. The ionization potential (10.52 eV.)[33] and the electron affinity (−1.81 eV.)[29] of the ethylene molecule and therefore, H_{PP} (7.49 eV.) and H_{QQ} (8.44 eV.) are different from those of cyclohexene. H_{VV} and H_{RR} are the observed $N\rightarrow V$ and $N\rightarrow R$ transition energies, 7.65 and 7.11 eV. respectively.[57,58] These four diagonal elements are larger than those for the cyclohexene complex. The other diagonal and all of the off-diagonal elements are just the same as were used for the cyclohexene complex.

With $C=-1.0$, the delocalization energy was evaluated to be 0.841 eV., which is smaller than that of the cyclohexene complex by 0.21 eV. This seems to mean that the silver ion complexes with ethylene and other simple monoölefins with higher ionization potentials may be more unstable than the cyclohexene-silver ion complex.

Although the effect of the anions of silver salts is disregarded in the present treatment, this is not the case experimentally. The cyclohexene-silver nitrate complex is stable only at a low temperature and no cyclohexene complexes have ever been known with silver salts other than the perchlorate and nitrate.[59] The different stabilities of these complexes seem to depend on the strengths of the interaction between the metal ions and the negative ions. Hence, the inability of silver chloride and sulfate to form complexes with cyclohexene may be explained by assuming that these anions have a strong affinity for silver cations.

Summary

The ultraviolet, infrared and Raman spectra of the cyclohexene-silver perchlorate complex

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[55] L. E. Orgel, "An Introduction to Transition-Metal Chemistry," Methuen & Co., London (1959), p. 67.

[56] Winstein and Lucas[3] showed the existence of olefin-silver complexes with a 2:1 ratio in aqueous media. The solid complex also has the same composition ratio.[14] In both cases, a silver ion is supposed to be stacked in between two olefin molecules.[9]

[57] P. G. Wilkinson and R. S. Mulliken, *J. Chem. Phys.*, **23**, 1895 (1955); G. Reid, ibid., **18**, 1299 (1950); D. F. Evans, *J. Chem. Soc.*, **1960**, 1735.

[58] R. S. Mulliken, *J. Chem. Phys.*, **33**, 1596 (1960).

[59] The possible existence of cyclohexene-silver fluoborate is anticipated.

TABLE XII. ELECTRONIC TRANSITION ENERGIES (IN eV.) OF CYCLOHEXENE AND ETHYLENE WITH VIBRATIONAL PROGRESSIONS (IN PARENTHESES, IN cm^{-1})

	V_{peak}	R_{OO}	T_{R}	T_{peak}
Cyclohexene	6.79	5.92 (1450)	4.9 (900)	3.8 (1200~1300)
Ethylene[27,57,58]	7.65 (850)	7.11 (1375)	6.4 (1400)	4.6 (~1000)
Electronic configration and spin multiplicity of the upper state	$^1(12)$	$^1(13)$	$^3(13)$	$^3(12)$

have been measured under various conditions. A new band has been found in the 220~230 mμ region for the complex in an aqueous solution; it has been found to have the mixing character of the charge-transfer from the olefin to the metal ion and of the Rydberg transition within the olefin molecule. The equilibrium constant (pK) has been evaluated spectrophotometrically as $0\sim-2$ for the equilibrium

$$C_6H_{10} + Ag^+ \rightleftharpoons C_6H_{10}\cdots Ag^+$$

The 1653 cm^{-1} $\nu(C{=}C)$ and 716 cm^{-1} $\delta(=\overset{|}{C}-H)$ bands of pure cyclohexene have been found to shift to about 1585 and 745 cm^{-1} respectively by means of complex formation with silver perchlorate, both in solids and in solutions. This and other facts concerning the vibration spectrum of the complex show that the C=C bond is weakened by the complex formation.

The very selective complex formation ability of Cu^+, Ag^+ and Hg^{2+} toward monoölefins has been explained by the calculation in which we explicitly took into account the charge number, the ionization potential, the electron affinity, the ionic radius, the hydration (solvation) energy, and the various atomic excitation energies of the ions. It has been pointed out that the roles of the d-electrons of the metal ion and the 3sσ-electrons of the olefin molecule are important in the ground state and the lowest excited state respectively, while the effect of the hydration (or lattice) energy is important in both states.

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Appendix I

The Various Electronic States of Cyclohexene.—The 209 mμ (5.92 eV.) band of cyclohexene was found, on the longer wavelength side, to have progressions with a vibrational frequency interval of about 1450 cm^{-1}. This band may possibly be assigned to be the Rydberg transition (N→R) on the basis of a comparison with the 7.11 eV. band of ethylene with 1375 cm^{-1} spacing so assigned by Mulliken.[57,58] Potts[27] observed the N→V transition of cyclohexene at 183 mμ (6.79 eV.), but he undertook no vibrational analysis. By measuring the spectrum of pure liquid cyclohexene with 1 cm. and 10 cm. cells, we have observed two different kinds of vibrational progressions in the longer wavelength region, namely, one around 4.9 eV. with 900 cm^{-1} spacings and another around 3.8 eV. with 1200~1300 cm^{-1} spacings. The former and the latter have tentatively been assigned to the Rydberg triplet (T_{R}) and the $\pi\rightarrow\pi^*$ triplet transition (T) respectively on the basis of the expected parallelism with the ethylene bands. There are doubts, however, about this assignment, because the magnitudes of their spacings are quite the reverse of those for ethylene and cyclohexene. Both triplet bands show the expected O_2-intensification and N_2-weakening, the effect being more pronounced for the longer wavelength one. Table XII lists the observed four transition energies of cyclohexene, along with the assignment for ethylene bands by Mulliken.[58]

Appendix II

Tables of Overlap Integrals.—The overlap integrals of the $S(3s, 3s)$, $S(3s, 5s)$ and $S(2p\pi, 5p\pi)$ types were calculated according to the standard method.[35-37,60] The results are shown in Table XIII—XV.

TABLE XIII. $S(3s, 3s)$

p	$t=0$	$t=0.125$	$t=0.25$	$t=0.5$
0.0	1.000	0.946	0.798	0.365
1.0	0.968	0.918	0.780	0.369
2.0	0.885	0.846	0.734	0.375
2.5	0.832	0.800	0.703	0.377
3.0	0.772	0.746	0.666	0.378
3.5	0.708	0.688	0.624	0.376
4.0	0.641	0.626	0.576	0.370
4.5	0.672	0.563	0.528	0.360
5.0	0.504	0.499	0.475	0.345
5.5	0.438	0.437	0.424	0.330
6.0	0.375	0.376	0.372	0.311
7.0	0.264	0.269	0.277	0.267
8.0	0.177	0.183	0.197	0.221
9.0	0.114	0.119	0.135	0.177
10.0	0.070	0.075	0.089	0.138

Appendix III

The Evaluation of Overlap Integral, Including d- and p-Orbitals with Distorted Conformation.—

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60) M. Kotani, A. Amemiya and T. Simose, *Proc. Math. Soc. Japan*, **20**, Extra No. 1, 1 (1938); M. Kotani, A. Amemiya, E. Ishiguro and T. Kimura, "Table of Molecular Integrals," Maruzen Co., Tokyo (1955).

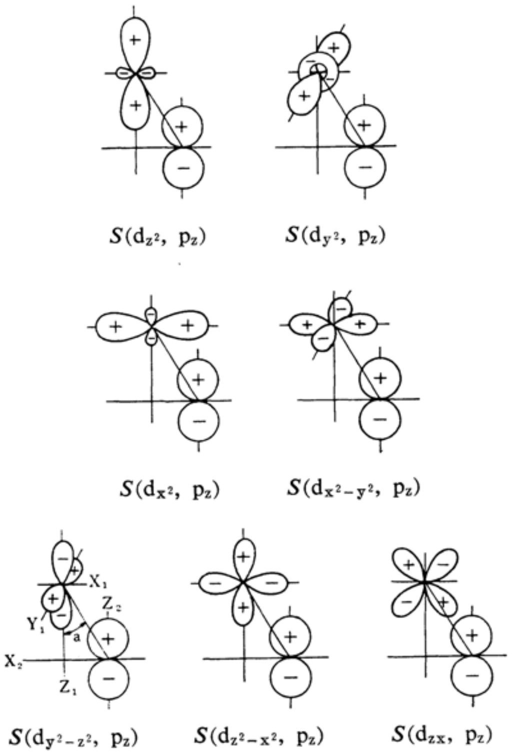
TABLE XIV. $S(3s, 5s)$

p	t						
	−0.5	−0.25	−0.125	0	0.125	0.25	0.5
0.0	0.513	0.933	0.996	0.935	0.775	0.560	0.171
0.5	0.512			0.930			0.173
1.0	0.510	0.910	0.961	0.914	0.759	0.566	0.178
1.5	0.506			0.888			0.186
2.0	0.502	0.850	0.900	0.855	0.730	0.555	0.196
2.5	0.496			0.816			0.208
3.0	0.489	0.767	0.806	0.772	0.681	0.540	0.220
3.5	0.479			0.724			0.231
4.0	0.467	0.670	0.693	0.672	0.610	0.511	0.241
4.5	0.453			0.618			0.249
5.0	0.435	0.565	0.576	0.562	0.527	0.464	0.254
5.5				0.505			
6.0	0.391	0.457	0.456	0.448	0.432	0.401	0.256
6.5				0.393			
7.0	0.340	0.354	0.346	0.340	0.333	0.330	0.246
7.5				0.291			
8.0	0.285	0.262	0.249	0.246	0.252	0.259	0.226
9.0	0.232	0.187	0.173	0.170	0.179	0.195	0.201
10.0	0.183	0.128	0.114	0.112	0.122	0.141	0.172
12.0		0.055	0.045	0.044	0.051	0.066	
14.0		0.021	0.016	0.015	0.019	0.028	
16.0		0.008	0.005	0.005	0.006	0.011	

TABLE XV. $S(2p\pi, 5p\pi)$

p	t						
	−0.5	−0.25	−0.125	0	0.125	0.25	0.5
0.0	0.802	0.973	0.891	0.732	0.539	0.350	0.089
0.5	0.794			0.726			0.090
1.0	0.770	0.931	0.855	0.707	0.525	0.346	0.091
1.5	0.731	0.883		0.677		0.341	0.093
2.0	0.681	0.812	0.755	0.635	0.484	0.330	0.095
2.5	0.622	0.736		0.584		0.316	0.096
3.0	0.559	0.652	0.612	0.526	0.416	0.296	0.097
3.5	0.494	0.569		0.464		0.275	0.096
4.0	0.431	0.483	0.455	0.401	0.330	0.249	0.094
4.5	0.371	0·405		0.341		0.223	0.091
5.0	0.316	0.336	0.316	0.284	0.245	0.196	0.087
5.5	0.266	0.287		0.234		0.170	0.082
6.0	0.223	0.218	0.205	0.189	0.170	0.125	0.076
6.5				0.151			
7.0	0.152	0.135	0.127	0.119	0.113	0.103	0.064
7.5				0.093			
8.0	0.102	0.081	0.075	0.072	0.071	0.069	0.052
8.5				0.055			
9.0	0.067	0.047	0.042	0.041	0.043	0.045	0.041
9.5				0.030			
10.0	0.043	0.026	0.023	0.023	0.025	0.028	0.031

For evaluating the matrix elements, we need to estimate the overlap integrals involving d- and p-orbitals in the assumed geometrical conformation of the complex. Let us consider the case in which the two xz planes of the metal (M) and carbon (C) atoms coincide with each other and in which the line (MC) joining the atoms is inclined at an angle α to the z axis. The overlap integrals for the various combinations shown in Fig. 10 between the d-orbitals of the atom M and the p_z-orbital of the atom C are expressed as linear combinations of $S(\sigma, \sigma)$ and $S(\pi, \pi)$ forms for which published



$S(d_{z^2},\ p_z)$ $S(d_{y^2},\ p_z)$

$S(d_{x^2},\ p_z)$ $S(d_{x^2-y^2},\ p_z)$

$S(d_{y^2-z^2},\ p_z)$ $S(d_{z^2-x^2},\ p_z)$ $S(d_{zx},\ p_z)$

Fig. 10. Various combinations of the d-orbitals of a metal atom and the p_z orbital of a carbon atom.

tables[35-37] are available. The results are as follows:

$$S(d_{x^2},\ 2p_z)=-1/4\cdot\cos\alpha\,(3\cos 2\alpha-1)\cdot S(d\sigma,\ 2p\sigma)$$
$$-\sqrt{3}/2\cdot\sin\alpha\cdot\sin 2\alpha\cdot S(d\pi,\ 2p\pi)$$
$$S(d_{y^2},\ 2p_z)=-1/2\cdot\cos\alpha\cdot S(d\sigma,\ 2p\sigma)$$
$$S(d_{z^2},\ 2p_z)=1/4\cdot\cos\alpha\,(3\cos 2\alpha+1)\cdot S(d\sigma,\ 2p\sigma)$$
$$-\sqrt{3}/2\cdot\sin\alpha\cdot\sin 2\alpha\cdot S(d\pi,\ 2p\pi)$$
$$S(d_{x^2-y^2},\ 2p_z)=\sqrt{3}/4\cdot\sin\alpha\cdot\sin 2\alpha\cdot S(d\sigma,\ 2p\sigma)$$
$$+1/2\cdot\sin\alpha\cdot\sin 2\alpha\cdot S(d\pi,\ 2p\pi)$$
$$S(d_{y^2-z^2},\ 2p_z)=-\sqrt{3}/2\cdot\cos^3\alpha\cdot S(d\sigma,\ 2p\sigma)$$
$$+1/2\cdot\sin\alpha\cdot\sin 2\alpha\cdot S(d\pi,\ 2p\pi)$$
$$S(d_{z^2-x^2},\ 2p_z)=\sqrt{3}/2\cdot\cos\alpha\cdot\cos 2\alpha\cdot S(d\sigma,\ 2p\sigma)$$
$$-\sin\alpha\cdot\sin 2\alpha\cdot S(d\pi,\ 2p\pi)$$
$$S(d_{xy},\ 2p_z)=S(d_{yz},\ 2p_z)=0$$
$$S(d_{zx},2p_z)=\sqrt{3}/2\cdot\cos\alpha\cdot\cos 2\alpha\cdot S(d\sigma,\ 2p\sigma)$$
$$+\sin\alpha\cdot\cos 2\alpha\cdot S(d\pi,\ 2p\pi)$$

It should be emphasized here that, unlike the p-orbitals, the d-orbitals are not vectoricaly decomposed into their x, y and z components; some authors[61] have wrongly evaluated the overlap integrals involving d-orbitals with distorted conformations. General formulations, their derivations, and the necessity for using auxiliary d_{x^2}, d_{y^2}, $d_{y^2-z^2}$ and $d_{z^2-x^2}$ functions will be described elsewhere.[62]

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61) D. A. Brown, *J. Chem. Phys.*, 33, 1037 (1960).

62) H. Hosoya, *Tech. Rept. ISSP* (The Institute for Solid State Physics, the University of Tokyo), Ser. B, to be published.