transition of composition A, a value of 4.73 ± 0.05 cal. deg.$^{-1}$ mole^{-1} (of components) is obtained. This differs from the sum of the entropy of transition of complex in composition A, of transition of excess cyclopentane in this composition and of solution of this excess cyclopentane in complex by only

$$4.88 \pm 0.01 - 4.73 \pm 0.05 = 0.15 \pm 0.06 \text{ cal. deg.}^{-1}\text{ mole}^{-1} \text{ (of components)}$$

This difference exceeds experimental accuracy; however it is felt that this discrepancy is probably due to the extrapolations involved to obtain entropies of transition in compositions A and B.

Thus, it appears that excess cyclopentane in composition A exists as a separate phase at the absolute zero and all disorder results from the five forms of complex randomly arranged in solid solution at this temperature. The occurrence of five isomers is certainly due to the non-planarity of the cyclopentane ring. Solution of excess cyclopentane in the complex begins as the temperature is increased and is almost completed at the rotational transition of the complex. The cyclopentane in solid solution is influenced by the complex to begin rotation at the rotational transition of the complex.

Note Added in Proof.—In calculating values of the entropies of the solutions from those of the components we have used the measured value of the entropy of gaseous cyclopentane at 298.16°K. and 1 atm.,[7] part of which was the entropy of vaporization calculated from a measured value of the heat. Kilpatrick, Pitzer and Spitzer[12] have pointed out that this value of the heat is inconsistent with the vapor pressure data, while a value calculated from the vapor pressure equation yields an entropy of the vapor which is more consistent with one calculated from reasonable spectroscopic and molecular data.

If the value of the entropy of ideally gaseous cyclopentane at 298.16°K. and 1 atm. recommended by Kilpatrick, Pitzer and Spitzer is used to calculate the entropy of the gaseous mixture the value obtained for solution B is 76.60 cal. deg.$^{-1}$ mole^{-1}, which is only 0.73 higher than the measured value. This difference is exactly (R ln 3)/3 (= 0.73). The value calculated for composition A is 0.44 cal. deg.$^{-1}$ mole^{-1} compared to (0.92 R ln 3)/3 (= 0.67).

It is possible that R ln 3 corresponds to three possible different orientations of the 2,2-dimethylbutane in the complex. It is of interest that a value of the entropy of the liquid of composition B calculated from the experimental values for the components at 298.16°K. using the ideal entropy mixing is 0.60 cal. deg.$^{-1}$ mole^{-1} higher than the experimental value. This is within experimental error of the difference found above (0.73). This might be considered as confirmation of the heat of vaporization calculated from the vapor pressures. It is hoped to make some new measurements in this laboratory to resolve this point.

The uncertainty in no way affects the arguments, based on the heat capacities concerning phase separation of the cyclopentane at low temperatures.

Acknowledgments.—We wish to thank Dr. D. M. Nace, Dr. J. G. Greyson, Mr. Q. R. Stottlemeyer and Mr. C. M. Knobler for their assistance with experimental measurements.

[12] J. E. Kilpatrick, K. S. Pitzer and R. Spitzer, THIS JOURNAL, **69**, 2483 (1947).

UNIVERSITY PARK, PENNA.

[CONTRIBUTION NO. 613 FROM THE INSTITUTE FOR ATOMIC RESEARCH AND DEPARTMENT OF CHEMISTRY, IOWA STATE COLLEGE. WORK WAS PERFORMED IN THE AMES LABORATORY OF THE U. S. ATOMIC ENERGY COMMISSION]

The Silver Perchlorate–Benzene Complex, $C_6H_6 \cdot AgClO_4$, Crystal Structure and Charge Transfer Energy[1]

BY HAROLD G. SMITH AND R. E. RUNDLE

RECEIVED APRIL 11, 1958

The silver perchlorate–benzene complex consists of –Bz–Ag–Bz–Ag– chains and perchlorate ions. The two silver ions associated with each benzene lie above and below the ring over bonds one and four of the ring. The silver ion positions are asymmetric and disordered, with Ag–C distances of 2.50 and 2.63 Å. to the two carbons of the nearest bond. The benzene ring is distorted; the two C–C distances nearest the silver ions are 1.35 Å., the four others are 1.43 Å. Evidently polarization of the π-bonding system leads to an increase in electron density in bonds nearest silver ions, and this is far more important than charge-transfer bonding in determining electron density within the ring. An attempt has been made to calculate the charge-transfer bond energy, using crystal energies as a guide. Our result is that the $\mathrm{Ag}\ldots\overset{\mathrm{C}}{\underset{\mathrm{C}}{|}}$ charge-transfer bond energy is ~15.7 kcal./mole, and our estimated errors are such as to suggest that this is an upper limit.

Introduction

Charge-transfer complexes, their stabilities, spectra and electronic structures have been of considerable theoretical and experimental interest.[2] Indeed, it has frequently been suggested that they play an important role as intermediates in reaction mechanisms.[3] Few such complexes have stabilities that permit direct observation of their structures, and of these, the most available is the silver perchlorate–benzene complex, $C_6H_6 \cdot AgClO_4$. The gross features of its structure have been given previously,[4] but an accurate refinement has revealed details about the benzene ring which appear to be important. In addition an accurate structure has permitted the calculation of the crystal lattice energy and an estimation of the energy of the charge-transfer bond which we believe is more reliable than those given previously.

Experimental Data

Single crystals of the silver perchlorate–benzene complex are obtained easily by dissolving silver perchlorate, either the anhydrous or the monohydrate, in liquid benzene and allowing the benzene to evaporate slowly. The crystals are usually flat plates or parallelopipeds and are stable under a vapor pressure of benzene but decompose rapidly when ex-

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[1] This paper is based in part on a thesis presented by Harold G. Smith to Iowa State College in partial fulfillment of the requirements for the Ph.D. degree, June, 1957.

[2] L. J. Andrews, *Chem. Revs.*, **54**, 713 (1954), reviews both experimental work and theory. See additional references therein.

[3] P. W. Robertson, P. B. D. de la Mare and W. T. G. Johnston, *J. Chem. Soc.*, 276 (1943); M. J. S. Dewar, *ibid.*, 777 (1946).

[4] R. E. Rundle and J. H. Goring, THIS JOURNAL, **72**, 5337 (1950).

posed to air, making it necessary to seal them in thin-walled glass capillaries for X-ray diffraction studies.

Timed exposures were taken of the [001] and [010] zones with a precession camera and Mo Kα radiation. Higher level data also were taken for qualitative interpretations. A few low-order reflections were affected by absorption, but these reflections did not seriously affect the two-dimensional refinements.

The three-dimensional data used in this investigation were taken on a Weissenberg camera with the a-axis as the axis of rotation. Mo Kα radiation was used and six layer lines were obtained. Absorption effects were not apparent in these data. In addition to the usual Lorentz-polarization corrections, the intensities also were corrected for the variation of spot size on the higher level Weissenberg photographs. This was done with the aid of the Phillips chart.[5]

The space group is Cmcm, Cmc2$_1$ or C2cm and the lattice constants are a = 8.35 Å., b = 8.02 Å. and c = 11.68 Å. The observed density is 2.4 g./cc. and, assuming four molecules per unit cell, the calculated density is 2.42 g./cc.

Structure Refinement.—The refinement was begun with the parameters determined by Rundle and Goring.[4] The R-factor, $R = \Sigma||F_0| - |F_c||/\Sigma|F_0|$, at this stage was 0.22 for the [100] zone. Although there was qualitative agreement for the [010] and [001] zones, the over-all agreement was not good. It was noticed that, in general, the observed structure factors of those reflections with h large were much weaker than the calculated structure factors. This indicated either a highly anisotropic temperature factor in the x-direction or a non-centrosymmetric space group which would permit x-parameters for silver, chlorine and all the oxygen atoms. The space group Cmc2$_1$ may be eliminated since this would allow the above atoms to have z-parameters and would make the ($00l$) reflections less intense than the ($h00$) reflections, contrary to observation. Space group C2cm allows silver, chlorine and oxygen atoms to have x-parameters, which is consistent with the observed data.

Although the space group C2cm is non-centrosymmetric, the (100) projection is centrosymmetric and, therefore, this zone was refined first. Synthetic and difference Fourier maps were used in the initial stages of refinement. One set of oxygen atoms was beneath a silver atom but was located fairly accurately by a Fourier map with the silver atoms subtracted out (Fig. 1). An over-all temperature factor B = 2.75 Å.^{2} was obtained from a semi-log plot of F_c/F_0 *vs.* $\sin^2\theta/\lambda^2$. This value did not change until individual temperature factors were included in the least squares refinement. The R-factor for the ($0kl$) reflections was reduced to 0.096.

The electron density projections on to (001) and (010) are not centrosymmetric for the space group C2cm. The peaks in the (001) Fourier projection, based on Cmcm, were quite elongated in the x-direction, suggesting that the silver, chlorine, and one set of oxygen atoms should lie off the mirror planes by about 1.5/60 to 2/60 of a. Structure factors calculated with these positions, however, did not improve the agreement with the observed ($hk0$) reflections and actually made matters worse for some reflections. A trial and error procedure was begun, and it was noticed that if the silver atoms alone were moved off the mirror plane and only the real part of the structure factor was considered, then the agreement between the observed and calculated structure factors was greatly improved. The best agreement was for x_{Ag} = 0.030 (about 0.25 Å.). This was equally true for the ($h0l$) data. The fact that the imaginary part of the structure factor had to be neglected indicated a disordered arrangement of the silver atoms; they must be considered as eight half-atoms in the eightfold set ($xy^1/_4$) of the centrosymmetric space group Cmcm.

A few three-dimensional structure factors that were quite sensitive to the silver positions were calculated and in all cases the agreement with the observed values was improved. It was felt that the structure was now accurate enough to begin a least squares analysis.

The least squares analysis was made using an IBM-650 Magnetic Drum Computer. The program, furnished by Drs. Senko and Templeton of the University of California, includes the calculation of structure factors and allows individual, but isotropic, temperature factors to be used. The ($0kl$) data were refined first, and after a few cycles the R-factor was lowered from 0.096 to 0.086. The resulting parameters were used to begin the three-dimensional refinement.

Scale factors for the individual layer lines were obtained from semi-log plots of F_c/F_0 *vs.* $\sin^2\theta/\lambda^2$. The relation between the individual layers was approximately linear and did not seem to indicate an over-all anisotropic temperature factor. The three-dimensional R-factor, calculated at the beginning of the least squares refinement, was 0.122 and after a few cycles decreased to about 0.094.

It was noticed that the temperature factor for oxygen (O$_1$) was steadily increasing and so two cycles were run with all the oxygen atoms in disordered positions slightly off the mirror planes. The oxygen atoms remained off the mirror planes and the temperature factor of oxygen (O$_1$) dropped from 5.7 to 5.0 Å.^{2}. The R-factor after the first cycle was again 0.094 and the structure refinement was considered complete. A total of 522 reflections, including some reflections too weak to be observed, were used in the refinement.

The final parameters and standard deviations, including temperature factors, are listed in Table I. The standard deviations for a given atom are larger in the x-direction than in the y- and z-directions, and this is attributed to a lack of data for larger values of h as compared to k and l. Bond distances and standard deviations are given

TABLE I

FINAL PARAMETERS AND STANDARD DEVIATIONS (PARAMETERS BASED UPON SPACE GROUP CMCM)

	x	y	z	B, Å.^{2}
Ag[a]	0.0313 ± 0.0003	0.0437 ± 0.0001	$^1/_4$	2.63
Cl	0	.4468 ± .0003	$^1/_4$	2.40
O$_1$[b]	0.0258 ± 0.0027	.3422 ± .0018	0.1511 ± 0.0017	5.07
O$_2$[b]	.1468 ± .0013	.5488 ± .0008	0.2647 ± 0.0009	3.45
C$_1$	.1720 ± .0017	0	0	2.60
C$_2$	.0811 ± .0010	0.8874 ± 0.0007	0.0687 ± 0.0005	2.29

[a] Half atoms in 8(g). [b] Half atoms in general set. O$_1$ can be placed in the mirror at x = 0, and O$_2$ in the mirror at z = $^1/_4$ without materially worse agreement, but with larger temperature factors.

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(5) D. C. Phillips, *Acta Cryst.*, 9, 819 (1956).

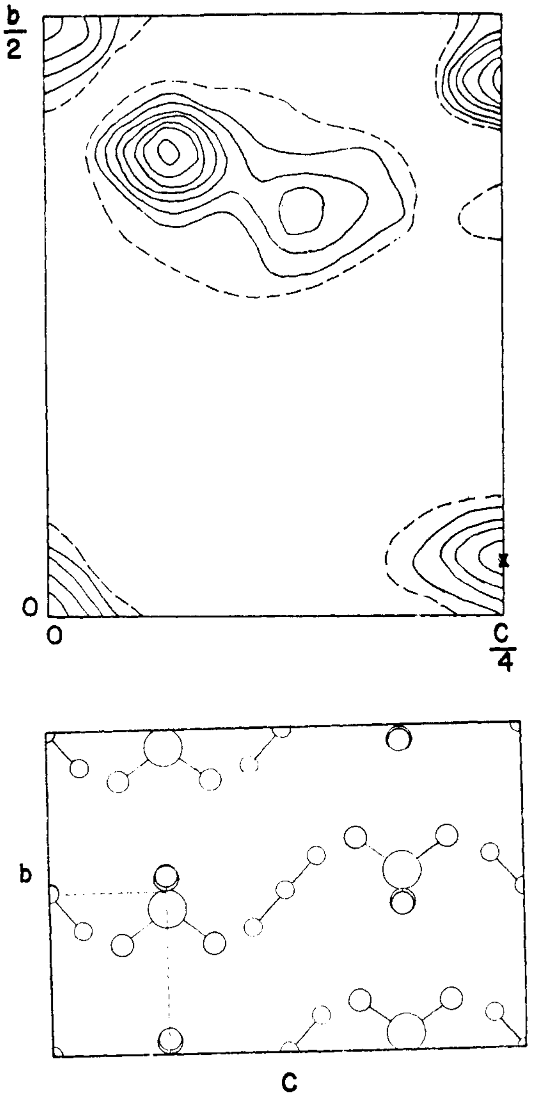

Fig. 1.—Electron density projection onto (100) with the silver atom (denoted by X) subtracted out. Projections of the atoms for one unit cell are shown in the smaller drawing. Carbon, oxygen, silver and chlorine atoms are represented by circles of increasing size.

in Table II along with some pertinent bond angles. A diagram of bond distances and bond angles is illustrated in Fig. 2. Aside from the disorder in the silver positions and detailed bond distances, the previous drawing of the structure is adequate.[4,6]

Discussion of the Structure

The final structure places the four silver atoms in the eightfold set ($xy^1/_4$) in a random manner. It may be argued that an anisotropic temperature factor (exponential function) for the silver atoms would also give good agreement with the observed data, and this is probably true for low values of h. However, a cosine function gives good agreement for low and high orders of h while an exponential function (temperature factor) gives good agreement for either the low orders or the high orders of h but not both, and this indicates that the equilibrium positions of the silver atoms are truly off the mirror planes.

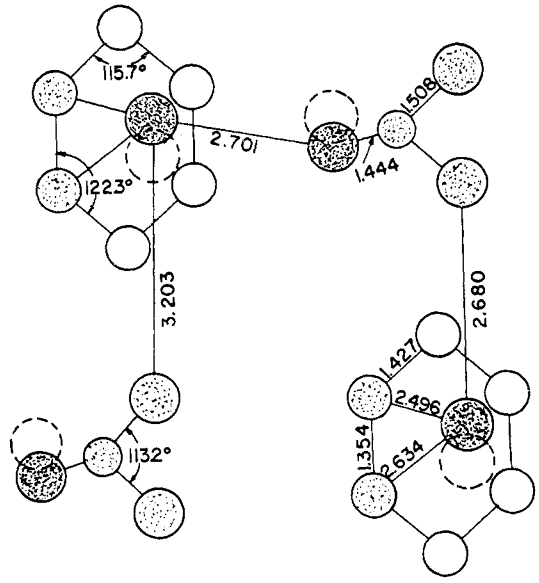

Fig. 2.—Diagram of bond distances and bond angles. The dashed circles indicate the alternate positions of the silver and oxygen atoms due to the disorder in the structure.

TABLE II

BOND DISTANCES AND BOND ANGLES

Ag^a–C	2.496 ± 0.006 Å.	C_2–C_2	1.354 ± 0.017 Å.
	2.634 ± .008	C_1–C_2	1.427 ± 0.010
Ag^a–O_1	2.658 ± .016	Cl–O_1	1.444 ± 0.018
	2.701 ± .016	Cl–O_2	1.508 ± 0.009
Ag^a–O_2	2.680 ± .011	$<O_1$–Cl–O_1	106.3°
	3.203 ± .011	$<O_2$–Cl–O_2	113.2°
		<Ag–Bz ring	101.0°
Ag–Cl	4.794 ± .002	<Bz–Ag–Bz	118.8°
	3.243 ± .002	$<C_2$–C_1–C_2	115.7°
	3.990 ± .003	$<C_1$–C_2–C_2	122.3°
	4.504 ± .003		

[a] The differences in bond distances in similar bonds are due to the disordered positions of silver. Oxygens were assumed to lie in mirror planes.

It is not readily apparent why the silver atoms should lie slightly off the mirror planes (or why their thermal motion should be much larger in the x-direction if this should be the case). The coördination about a silver atom in the neighborhood of the $x = 0$ plane is fairly compact. On one side of the silver atom it is coördinated to four carbon atoms at about 2.55 Å., and on the other side to two oxygen atoms at about 2.68 Å. If the silver atoms were in the mirror plane the silver–oxygen distances in the x-direction would be 2.94 Å. whereas it actually is 3.20 Å. on one side and 2.68 Å. on the other. It is not believed, however, that this is an indication of silver–oxygen bonding because the distances are still quite long.

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(6) A table of the observed and calculated structure factors has been deposited as Document number 5592 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the Document number and by remitting $1.25 for photoprints, or $1.25 for 35 mm. microfilm in advance payment by check or money order payable to: Chief, Photoduplication Service, Library of Congress.

Helmholz and Levine[7] have attributed the color of silver phosphate, Ag_3PO_4, and silver arsenate, Ag_3AsO_4, to silver–oxygen bonding, but there the silver–oxygen distances are 2.34 Å. It is perhaps significant that the above authors found it necessary to ascribe a large anisotropic thermal motion to the silver atoms in order to obtain good agreement with the observed intensities.

The perchlorate ion is somewhat distorted from an ideal tetrahedron with unequal chlorine–oxygen distances, $Cl–O_1 = 1.44$ Å. and $Cl–O_2 = 1.51$ Å., as well as unequal bond angles, $O_1–Cl–O_1 = 106.3°$ and $O_2–Cl–O_2 = 113.2°$. The shorter Cl–O bond occurs on the side of the ion with the shortest silver–chlorine distance and probably is due to polarization by the silver ion. Similar bond distances and bond angles exist in the perchlorate ion in potassium perchlorate.[8]

It is not possible to say at this time whether the oxygen atoms are truly off the mirror planes in disordered positions or whether the motion of the perchlorate group is anisotropic since the oxygen atoms do not influence the intensities of the reflections as much as the silver atoms. However, it would not be surprising if the displaced oxygen atoms in this case represent a true thermal motion, for many perchlorate ions are believed to undergo free rotation in solids at higher temperatures, and recently it has been shown[9] that the perchlorate group in the silver perchlorate–dioxane complex is rotating at room temperature.

An interesting result of the three-dimensional refinement is the distortion of the benzene molecule by the crystal field. Instead of 120° for all the interior angles of the ring, two are 115.6° and four are 122.2°. The distance between the two carbon atoms in the ring nearest the silver atoms is 1.35 Å. while the neighboring carbon–carbon distance is 1.43 Å.

Although the silver ion is considered to be an electron-acceptor in the silver perchlorate–benzene complex, the small amount of charge that is believed to be transferred from the ring to the ion is not expected to change the bond distances appreciably, and even if they were altered it would be in the opposite direction to that observed.

Since the π-electrons of the benzene molecule are known to be quite mobile, a likely explanation for the change in bond distances in the molecule may be the polarization of the π-electrons by the positive silver ions on opposite sides of the molecule, increasing the electron density in the bonds nearest the positive silver ion.

According to valence bond theory,[10] the short and long bonds correspond to 77% and 30% double-bond character, respectively. In molecular orbital terminology[11] the short bond has a bond order of 1.80 and the long bond a bond order of 1.55. The bond order of benzene is 1.67.

Charge-transfer Energy.—As an aid in computing the charge-transfer energy, the formation of the silver perchlorate–benzene complex from silver perchlorate and liquid benzene may be considered to occur in two steps

$$AgClO_4(s) + Bz(l) \longrightarrow AgClO_4(ex) + Bz(ex) \longrightarrow AgClO_4 \cdot C_6H_6(s)$$

The intermediate step represents anhydrous silver perchlorate expanded to the lattice of the benzene complex as well as benzene expanded to the volume it occupies in the complex. The final step represents the inclusion of the benzene molecules into the voids of the lattice. The energy involved in the first step is the difference in lattice energies of silver perchlorate in the normal and expanded states plus the energy required to partially separate the molecules in liquid benzene. The energy gained by the inclusion of benzene in the lattice (second step) is assumed to be equal to the van der Waals energy, plus the benzene-crystal field interaction energy (ion-induced dipole interaction) and the charge-transfer energy between silver and benzene. The sum of the energies involved in the two steps should be equal to the heat of formation of the benzene complex, which is 8.1 kcal./mole.[12]

The calculation of the interaction energies of the silver and perchlorate ions in anhydrous silver perchlorate and in the silver perchlorate–benzene complex follows closely the procedure used by Mayer in his calculations of the lattice energies of the silver halides.[13] It is assumed that the charge transferred from benzene to silver is small and will not appreciably affect the electrostatic energies.

Anhydrous silver perchlorate exists in two forms, the high temperature modification ($T > 150°$) has the sodium chloride structure where the perchlorate ions are either rotating or statistically arranged to exhibit O_h symmetry,[14] and the low-temperature form has the orthorhombic $CaSO_4$ structure.[15] The Madelung constant for the latter structure has been calculated by Sakamoto to be 3.376.[16] The Madelung constant for the NaCl type structure is well known ($A_a = 3.495$). The Madelung energies of the two forms of silver perchlorate are not very different (162 kcal./mole for the orthorhombic and 167 kcal./mole for the cubic) and it is assumed that the difference in their total lattice energy is also small. (The heats of transition for similar compounds are about 3 kcal./mole.) The lattice energy of the cubic form is much simpler to calculate due to its high symmetry and the calculation may well be more reliable since the interatomic distances in the orthorhombic phase are not known precisely. Use of the higher Madelung energy increases the estimate of the charge-transfer energy and our estimates are consistently in the direction of putting an upper limit on that value. The cubic form, therefore, was considered in these calculations.

Considering only the Ag^+ and ClO_4^- ions, the Madelung constant for the expanded orthorhombic

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(7) L. Helmholz and R. Levine, THIS JOURNAL, **64**, 354 (1942).

(8) R. W. G. Wyckoff, "Crystal Structures," Vol. II, Interscience Publishers, Inc., New York, N. Y., 1951, Table VIIIA, pp. 9 and 10.

(9) R. J. Prosen and K. N. Trueblood, *Acta Cryst.*, **9**, 741 (1956).

(10) L. Pauling, "Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1940, p. 174.

(11) C. A. Coulson, "Valence," Oxford University Press, Oxford, 1952, p. 253.

(12) B. D. Tiddlesby and A. G. Sharpe, *Research*, **6**, 51 S (1953).

(13) J. E. Mayer, *J. Chem. Phys.*, **1**, 327 (1933).

(14) K. Herrmann and W. Ilge, *Z. Krist.*, **75**, 31 (1930).

(15) H. G. Smith, unpublished work, Iowa State College.

(16) Y. Sakamoto, *Bull. Chem. Soc. Japan*, **26**, 283 (1953).

benzene complex was computed by Ewald's[17] method and was found to be 3.453. The cube-root of the unit cell volume is 9.21 Å. and the corresponding Madelung energy is 124 kcal./mole.

In the calculation of the repulsive energies between the ions, the constants used by Mayer[13] for the silver and halide ions were also used in this investigation for the silver and perchlorate ions, *i.e.*, the perchlorate ion was considered to be similar to a halide ion. The radius of the perchlorate ion (2.36 Å.) is the "thermochemical" radius reported by Kapustinski[18] and was corrected to the Huggins and Mayer scale.[19] The repulsive energies between the ions in the normal and expanded states are 11.0 and 3.4 kcal./mole, respectively.

The dispersion energies (induced dipole–induced dipole interactions) between the ions were calculated by the approximate formula given by London in terms of the electronic polarizabilities of the ions and their principal electronic absorption energies.[20] Following Mayer,[13] the absorption energy for silver was taken to be 90% of the second ionization potential of the neutral atom. The observed ultraviolet absorption energy of the perchlorate ion is about 6 e.v.[21] The polarizability of the silver ion ($\alpha = 2.4$ Å.^{3}) has been calculated by Tessman, Kahn and Shockley[22] from the refractive indices of the silver halides. We have calculated the polarizability of the perchlorate ion in a similar manner for potassium, rubidium, cesium and ammonium perchlorate and the average value is 4.65 Å.^{3}. The dispersion energies of silver perchlorate in the normal and expanded states are −8.8 and −2.8 kcal./mole, respectively.

The energy of induction due to the induction of moments in an atom, molecule or ion by the electric field which arises from neighboring charge distributions is discussed in some detail by Hirschfelder, Curtiss and Bird.[23] For the cubic form of silver perchlorate, the induction energy is considered negligible since the field at the center of the ions is zero and therefore the dipole moments are zero and the energy of the induced multipole moments should be small. For the benzene complex the energy of induction between the silver and perchlorate ions is not negligible since the fields do not vanish at the center of the ions. The resulting energy is −3.4 kcal./mole.

The energy difference between the normal and expanded states of silver perchlorate is 38 kcal./mole and the energy required to expand liquid benzene to the volume of the expanded lattice is estimated to be about 60% of the heat of vaporization of benzene or 4.4 kcal./mole. The energy expended in the first step of equation 1 is, therefore, 42.4 kcal./mole (Table III).

TABLE III

	Lattice energies, kcal./mole $AgClO_4$ (cubic)	 $AgClO_4$ (expanded)
Madelung	−167.2	−124.2
Repulsive	+ 11.0	+ 3.4
Dispersion	− 8.8	− 2.8
Induction	0.0	− 3.4
	−165.0	−127.0

$AgClO_4 \rightarrow AgClO_4$ (expanded), $\Delta H = +38.0$ kcal./mole

Benzene(liq.) → benzene (expanded), $\Delta H = +4.4$

$\Delta H = +42.4$ kcal./mole

	Interaction energies, kcal./mole
Induction	−12.4
van der Waals	− 6.8
Charge transfer (by diff.)	−31.3
Step II ΔH =	−50.5

ΔH for steps I + II = $-50.5 + 42.4 = 8.1$ kcal./mole

Ag–Bz bond energy = $31.3/2 = 15.7$ kcal./mole

The energy gained by the inclusion of benzene in the expanded lattice should be this 42.4 kcal./mole plus the heat of formation of the complex, which gives a total of 50.5 kcal./mole. It is assumed that this is equal to the induction, van der Waals and charge-transfer energies of the benzene molecules due to the interactions with their neighbors.

The induction energy of benzene due to the crystal field was obtained by calculating the interaction energies of the individual bonds with the field. The electric fields were calculated midway between carbon atoms for the C–C bonds and at the carbon atoms for the C–H bonds. In most cases the resultant field was calculated from the contributions of the nearest eighteen ions. The anisotropic bond polarizabilities of Denbigh[24] were used. Because of the crystal symmetry it was necessary to determine the energies of only four bonds. The induction energies of the individual bonds varied from 0.78 to 1.23 kcal./mole. The total induction energy of the benzene molecule is −12.4 kcal./mole.

Coulson, Maccoll and Sutton have discussed the field dependence of the molecular polarizability of benzene in strong uniform fields.[25] Although the field strengths in the silver perchlorate–benzene complex are large, they are far from uniform and, therefore, it was considered best to use the low-field strength polarizabilities. Any error is probably in the direction of minimizing polarization and hence maximizing the charge-transfer energy.

Since the benzene ring is not spherically symmetric, the van der Waals interactions (dispersion and repulsion) of benzene with its neighbors are difficult to calculate.

It seems reasonable to suppose that the van der Waals interaction between benzene and silver perchlorate will regain the 4.4 kcal./mole for expansion of the benzene and exceed it by about the heat of fusion of benzene (2.4 kcal./mole). Hence, 6.8 kcal./mole has been taken as the value of the van der Waals energy.

The zero point energies have been neglected because they are usually small and the difference in

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(17) P. P. Ewald, *Ann. Physik*, **64**, 253 (1921).

(18) A. F. Kapustinski, *Quart. Rev. (London)*, **10**, 283 (1956).

(19) J. E. Mayer and M. L. Huggins, *J. Chem. Phys.*, **1**, 643 (1933).

(20) F. London, *Trans. Faraday Soc.*, **33**, 8 (1930).

(21) M. Wolfsberg and L. Helmholz, *J. Chem. Phys.*, **20**, 837 (1952).

(22) J. R. Tessman, A. H. Kahn and W. Shockley, *Phys. Rev.*, **92**, 890 (1953).

(23) J. O. Hirschfelder, C. F. Curtiss and R. B. Bird, "Molecular Theory of Gases and Liquids," John Wiley and Sons, Inc., New York, N. Y., 1954, p. 988.

(24) K. G. Denbigh, *Trans. Faraday Soc.*, **36**, 936 (1940).

(25) C. A. Coulson, A. Maccoll and L. Sutton, *ibid.*, **48**, 106 (1952).

zero point energies for the normal and expanded lattices should be even smaller.

The sum of the van der Waals energy and the inductive energy is 19.2 kcal./mole. This value subtracted from 50.5 kcal./mole is the estimate of the charge-transfer energy between the silver ions and the benzene molecules (Table III). This 31.3 kcal./mole represents the energy of a silver ion bonded to two benzene molecules; therefore, the energy per bond is 15.7 kcal./mole.

Although the errors involved in these calculations are probably large, most of the more uncertain quantities, such as van der Waals and induction terms, are relatively small and tend to cancel for the two step process used in the calculation. The Madelung energy difference between the expanded and normal $AgClO_4$ structures is probably quite accurate and is the principal term. The authors believe these results are more reliable than the rough estimate of 50 kcal./bond mole by Tiddlesby and Sharpe.[12] Their value is based upon the questionable assumption that most of the lattice energy of silver perchlorate is lost in forming the charge-transfer complex, a result dependent upon estimating ion pair interactions in solution. This estimate is surely of less accuracy than the Madelung energy difference computed here.

The charge-transfer bond energy found in this investigation is of the order of the van der Waals and induction energies in agreement with Mulliken's prediction of the magnitude of the charge-transfer interaction.

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AMES, IOWA

[CONTRIBUTION FROM THE W. A. NOYES LABORATORY OF CHEMISTRY, UNIVERSITY OF ILLINOIS]

Isotopic Exchange Reactions. IV. Evidence for the Tetrachloroborate Anion from Kinetic Studies[1]

BY ROLFE H. HERBER

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The halogen exchange between BCl_3 and a number of chloride salts has been studied in both the liquid and gas phase using Cl^{36} as a radiotracer. The heavy alkali metal salts do not undergo exchange at 0° in several hours. LiCl shows a small amount of halogen transfer in liquid BCl_3. Both $(CH_3)_4NCl$ and $(CH_3CH_2)_4NCl$ solutes exchange chlorine rapidly with liquid BCl_3 and the exchange with the former has been exploited to prepare radiochlorine labelled BCl_3. Silicon tetrachloride and trimethylchlorosilane do not exchange halogens with BCl_3 in the gas phase, although the latter should form a 1:1 addition compound with boron trichloride. These results are interpreted on the basis of an ionic mechanism which involves the formation of the tetrachloroborate anion in BCl_3 solution.

In a recent communication,[2] Muetterties has reported the preparation of a number of alkali metal salts of the unknown tetrachloroboric acid, $HBCl_4$. $KBCl_4$, $RbBCl_4$ and $CsBCl_4$ were recovered from a reaction vessel heated to 400 to 500° for 0.5 hr. and then cooled over a period of 8 hr. During this cooling period, the alkali metal salt was presumably in contact with liquid BCl_3, and hence the metathesis may have taken place either under gas–solid or liquid–solid heterogeneous reaction conditions. These results are of considerable interest in their relation to studies of isotopic exchange reactions of several volatile inorganic halides being carried out in this Laboratory, especially to work involving liquid and gaseous BCl_3.

The present study was undertaken to explore the possibility that BCl_4^- may be a reactive intermediate in isotopic exchange reactions of BCl_3, and to elucidate the conditions under which this anion may be formed.

Experimental

Tetramethylammonium Radiochloride.—The chlorine labeled reagent was prepared by dissolving E. K. white label grade salt in a minimal volume of water, adding an aliquot of HCl^{36} [3] and evaporating to dryness under high vacuum conditions. Subsequent pumping on this (and the following) salt while warmed to 100° was continued until static vacua of 10 μ or less were attained in all cases except the tetraethylammonium chloride, which has an m.p. of 37.5°.

Tetraethylammonium Radiochloride.—The unlabeled salt was prepared by neutralizing an aqueous 10% solution of Eastman Kodak tetraethylammonium hydroxide with HCl and evaporating to dryness. The chlorine labeled salt was prepared as above.

Alkali Metal Halides.—Lithium, rubidium and cesium chloride salts were reagent grade chemicals used without further purification. Chlorine-36 labeling was carried out as above.

Boron Trichloride.—Matheson 99% BCl_3 was freed of permanent gas impurity by alternate freezing, pumping and liquefaction cycles under high vacuum conditions. HCl was removed by warming the BCl_3 to −78° and pumping. Middle fractions of the purified gas were stored in glass ampoules. Chlorine-36 labeled BCl_3 was prepared from tetramethylammonium radiochloride on the basis of the results of the present work.

Chlorosilanes.—Silicon tetrachloride and trimethylchlorosilane were General Electric Co. reagents. Chlorine-36 labeled silanes were prepared as detailed in a previous communication.[4]

Exchange Run Procedure.—The experimental method used to follow the isotopic exchange kinetics was essentially that employed in previously reported[5] work. The gas-phase exchange runs (using $SiCl_4$ and $(CH_3)_3SiCl$) were carried out in 300-cc. Pyrex reaction flasks. The reactants were maintained at 24.0 ± 0.5 or 30.0 ± 0.5° in a water-bath and complete volatilization was noted within 10 seconds. Separation of BCl_3 from the chlorosilanes for radioassay was effected by cooling the reactants in a slush bath of *n*-hexanol (−50°). Since the vapor pressures of $SiCl_4$ and

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(1) This work supported by the U. S. Atomic Energy Commission. Presented in part as paper 132, Division of Physical Chemistry, San Francisco Meeting Am. Chem. Soc., April, 1958.

(2) E. L. Muetterties, THIS JOURNAL, **79**, 6563 (1957).

(3) Item Cl-36-P, available from Oak Ridge National Laboratory, Oak Ridge, Tennessee.

(4) R. H. Herber, *J. Phys. Chem.*, **62**, 379 (1958).

(5) R. H. Herber and A. W. Cordes, *J. Chem. Phys.*, **28**, 361 (1958).