$$k_2 = 2.57 \times 10^8\, e^{-320/RT}\ \text{l.}^2\ \text{mole}^{-2}\ \text{sec.}^{-1}$$

The result is in reasonably good agreement with the value obtained by Benson and Axworthy[16]

$$k_2 = 6.00 \times 10^7\, e^{+600/RT}\ \text{l.}^2\ \text{mole}^{-2}\ \text{sec.}^{-1}$$

The ΔE of reaction 3a is $25.4 - RT$ or 24.6 kcal. The activation energy for reaction 3a is 24.3 kcal. Therefore the conclusion is warranted that the reaction proceeds, as expected for atomic reactions of this type, with little or no positive energy of activation. It is in fact possible[16] that a small negative activation energy is actually involved in this energy transfer reaction.

Small deviations (on the high side) of the experimental rate obtained by Glissman and Schumacher[15] have been attributed by Benson and Axworthy[16] to the presence of thermal gradients in the reactor. No evidence for this hypothesis exists in the pressure range of the present ozone systems operating between 115 to 130°.

Conclusions

The thermal decomposition of concentrated ozone follows second order kinetics over the temperature range 70 to 130°. There is little deviation in the observed rate constant over the first 35% decomposition.

The data obtained in this research are in excellent agreement with the data previously reported by Glissman and Schumacher[15] and Benson and Axworthy.[16] When concentrated ozone decomposes, a steady state concentration of oxygen atoms rather than an equilibrium concentration is present.

Support is given for a modified Jahn mechanism of ozone decomposition suggested by Benson and Axworthy,[16] Schumacher[22] and Garvin.[21]

From the best available thermodynamic data values for k_2 have been calculated.

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NEW HAVEN, CONN.

[CONTRIBUTION FROM THE RICHARD B. WETHERILL LABORATORY OF CHEMISTRY, PURDUE UNIVERSITY, LAFAYETTE, INDIANA]

Nuclear Magnetic Resonance Line Shifts of Fluorine in AgF and Ag_2F[1,2]

BY Q. WON CHOI[3]

RECEIVED NOVEMBER 12, 1959

A new method of preparing silver fluoride solution without any contamination is described and a procedure for preparing very finely divided silver subfluoride is given. Nuclear magnetic resonance absorption lines are shifted by +0.014% and −0.009% for AgF and Ag_2F, respectively, with respect to the fluorine resonance line in KF aqueous solution. The positive shift corresponds to the higher magnetic resonant field at constant frequency. Possible interpretations for these data are provided.

Introduction

The magnetic resonance frequency of a given nucleus varies with its electronic environment. This arises because, as an external magnetic field H_0 is applied to an atom or molecule, its electrons acquire an induced diamagnetic circulation which produces a magnetic field $-\sigma H_0$ at the position of nucleus, partly cancelling the applied field. As pointed out by Ramsey,[4] the second-order paramagnetism partly cancels the diamagnetic shielding effect. Saika and Slichter[5] and Yosida and Moriya[6] correlated the contribution of the second order paramagnetism in an ionic compound with its degree of covalency of the binding. Gutowsky and McGarvey[7] have studied the resonance absorption spectra of Rb^{187} and Cs^{133} nuclei in various halides and have confirmed the parallel relation between the values of the relative line shift and the electronegativity differences of the metal and halogen involved. Yosida and Moriya[6] have found good agreement between their calculated values of shifts for halogen nuclei in alkali halides and the experimental results of Kanda.[8] In metallic conductors, however, there is another type of paramagnetic effect caused by the contact interaction of the conduction electron and the magnetic nuclei, known as the Knight shift.[9]

The F^{19} resonance shifts reported here appear to be the first provided for AgF and Ag_2F crystals. The n.m.r. study of the F^{19} nucleus in Ag_2F crystals is of particular interest since the compound is quite metallic in character, judging from measurements of the electrical resistivity[10] and of magnetic susceptibility.[11]

Experimental

Preparation of Pure AgF Solution.—The procedure adopted here is a modification of the one developed by Tapilov and Abdulaev[12] which consists of dissolving silver oxide, obtained by the oxidation of metallic silver with hydrogen peroxide, in hydrofluoric acid. Since hydrogen peroxide decomposes very readily in the presence of silver oxide, it is difficult to adjust the conditions so as to assure complete oxidation. In order to avoid such a difficulty, the silver

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(2) This work was supported by a grant from the Research Corporation.

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metal was dissolved in hydrofluoric acid by adding hydrogen peroxide; *i.e.*, the two-step procedure of Tapilov and Abdulaev was combined into one step. This modification makes the reaction very smooth and easily controllable.

Procedure.—Silver was prepared in a powdered state by reducing a concentrated solution of silver nitrate with ammonium formate.[13] In order to obtain the silver in a very finely divided state, ammonium formate solution was added very rapidly to the silver nitrate solution kept at 60°; the solution was then heated on a steam-bath.

A weighed portion of dry silver powder was moistened with one and one-half times the quantity of 25% hydrofluoric acid needed to convert the silver to silver fluoride. To this mixture, a 6% hydrogen peroxide solution was added dropwise over a period of at least 1 hr. The mixture was constantly agitated to avoid violent evolution of oxygen which might be caused by a local concentration of hydrogen peroxide. In order to dissolve the silver completely, about one and one-half the theoretically needed quantity of hydrogen peroxide was required. In the last stage of the reaction, there remained some brownish precipitate which could not be dissolved readily. Similar residues were obtained when a commercially available silver oxide was treated with an excess of hydrofluoric acid. Thus, it is not necessary to add more hydrogen peroxide if the resultant solution fails to become clearer. In order to expel the excess HF and to decompose the unreacted H_2O_2, the resultant solution was heated on a steam-bath for approximately 1 hr. until the gas evolution ceased. The brown precipitate was separated by filtration and the filtrate was concentrated on a steam-bath until a thin scum covered the solution.

Since the small quantity of free hydrofluoric acid in silver fluoride solution did not affect the further preparation of Ag_2F, the solution obtained above was ready for use after dissolving the scum with the least amount of water. However, if anhydrous silver fluoride is to be prepared from the solution, the excess HF must be expelled by continued evaporation, until the residue is virtually dry. In this case, silver fluoride can be obtained following the procedure developed by Anderson and Bak[14]: namely, by addition of methanol and ether in succession to the saturated solution of AgF.

Preparation of Ag_2F in a Finely Divided State.—In order to obtain Ag_2F crystals in a very finely divided state, the usual procedure[10,15] was modified as follows:

About one-third of the amount of silver used in the above-mentioned preparation was added to the silver fluoride solution prepared as described above. The mixture then was heated at about 50° overnight. It was necessary to break the scum formed on the liquid surface from time to time, to facilitate the evaporation of the solution so that the concentration of AgF could be kept as high as possible. Most of the silver metal added was converted to fairly coarse Ag_2F crystals. The supernatant solution was decanted and kept aside, while the residue was treated with the least possible amount of water necessary to decompose the silver subfluoride. The decomposition of Ag_2F by the action of water took place instantaneously and the silver formed was found to be in an extremely fine state of division. To this suspension of metallic silver in silver fluoride solution, the mother liquor that had previously been decanted was added, and the material then was warmed to about 40° in the dark for at least 5 hr. The silver fluoride solution now was decanted and the Ag_2F crystals were washed with absolute methanol six times. The Ag_2F was freed from methanol by keeping it in a desiccator in the presence of BaO, $CaCl_2$ and NaF under a moderate vacuum for about three days. Anhydrous AgF can be recovered from the mother liquor of the Ag_2F crop by use of methanol and ether, as mentioned before.

More than one-third of the Ag_2F crystals obtained passed the No. 200 sieve. It is noteworthy that Ag_2F thus obtained is not affected by light when kept in a sealed ampoule.

Determination of the N.m.r. Shifts.—The fine crystals of Ag_2F that passed the No. 200 sieve were embedded in solid paraffin in a Pyrex container so that the individual particles are electrically insulated. Any coarser Ag_2F particles lowered Q of the tank circuit of the radiofrequency oscillator to the extent that oscillation could not be sustained.

The magnet used is a twelve inch electromagnet, Varian model V-4012A-HR. The electronic equipment used to detect the nuclear resonance absorption was essentially the same as that developed by Pound, Knight and Watkins.[16] It employs a radio-frequency oscillator, amplifier and detector; the audio output of this unit was viewed directly on a cathode-ray oscilloscope or sent to a lock-in amplifier and a recorder. The coil of the radio-frequency oscillator was kept in the magnet air gap at a certain position and only the samples were exchanged. Since the time variation of the magnetic field was found to be smaller than the over-all experimental error of the present measurement, 25 p.p.m., the intensity of the applied magnetic field can be considered to be the same for different substances studied in a set of experiments. A National receiver model HRO-60 with National XCU-50-2 Crystal Calibrator Unit was used to determine the 100 kcps. marker positions. Since only the relative shifts were of interest, the crystal calibrator was calibrated only occasionally with WWV broadcasting.

The nuclear resonance frequency was determined by interpolation on the recorder strip chart, assuming the rates of chart drive and the frequency change of the oscillator were both linear. In order to minimize error, the external magnetic field was adjusted so that the nuclear resonance signals were located very closely to one of the 100 kcps. markers. Figure 1 shows an example of the recordings. Some of the measurements were carried out by obtaining the resonance signals with only one 100 kcps. marker, in order to minimize the time interval required for determining the relative shifts of two samples. Then the maximum nuclear absorption frequencies were calculated by using the predetermined distance between the two adjacent 100 kcps. markers. This type of experiment confirmed the negligible time drift of the external magnetic field. Figure 2 shows an example of such an experiment. The time constant used for detector output was kept smaller than 16 sec., since the time required to traverse the region between the maximum and minimum slopes of the signal was about 100 sec.

The resonance frequency of Ag_2F crystals was measured relative to that of AgF crystals and the measurement for the latter was made relative to the resonance frequency of 35% aqueous KF solution. The results are shown in Table I, together with the data for other fluorine compounds reported by Dickinson[17] and Gutowsky and Hoffman.[18]

TABLE I

RELATIVE SHIFT OF NUCLEAR MAGNETIC RESONANCE OF F^{19} IN VARIOUS COMPOUNDS

Compounds	Relative shift F_2 as reference	× 10^4 KF aqueous as reference
AgF	6.88[a]	1.40
HF (anhydrous)	6.25	0.77
HF (aqueous solution) and		
$BF_3 \cdot O(C_2H_5)_2$	5.85[b]	.43[b]
KF (aqueous solution)	5.48	.00
$C_2F_3Cl_3$	5.03[b]	− .45[b]
CF_4	4.91	− .57
Ag_2F	4.58[a]	− .90[a]
ClF_3	3.43	−2.05
F_2	0.00	−5.48

[a] This work; [b] Dickinson.[17] Others, Gutowsky and Hoffman.[18]

The line widths are measured between the maximum and minimum of the derivative curve and found to be 3.3 and 4.3 gauss for AgF and Ag_2F, respectively. Since the resonance signal from Ag_2F crystals was obtained by operating at higher radiofrequency oscillation levels, the line width for that compound may be in error.

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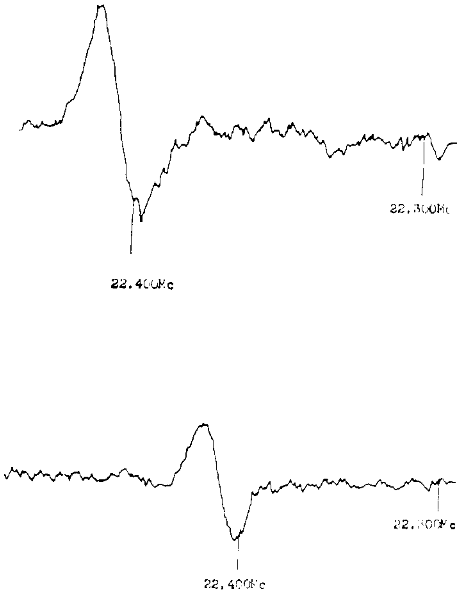


(a) AgF, 22.404_4Mc. (b) Ag_2F, 22.409_8Mc.

Fig. 1.—F^{19} resonance signals from AgF and Ag_2F with two 100 kc. markers.

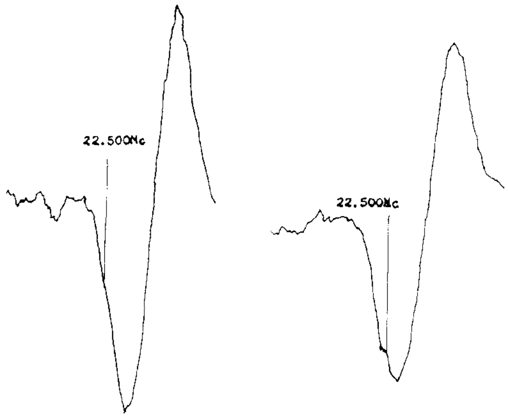
Discussion

The result[4–6] of the approximation applied to Ramsey's theory is

$$\Delta\sigma = -\lambda\frac{2}{3}\cdot\frac{e^2\hbar^2}{m^2c^2}\cdot\frac{1}{\Delta E}\cdot\left(\left\langle\frac{1}{r^3}\right\rangle_{\text{av}}\right)^0_{2\text{p}} \qquad (1)$$

where $\Delta\sigma$ is the relative size of the second-order paramagnetism with respect to an isolated fluorine ion as the reference state, ΔE is the average excitation energy of the molecule and $\left(\left\langle\frac{1}{r^3}\right\rangle_{\text{av}}\right)^0_{2\text{p}}$ is the average of $\frac{1}{r^3}$ for the valence electron of a free fluorine atom, and λ is the degree of covalency of the bond associated with the 2p electron. In the case of AgF crystals, where the shift of n.m.r. line is found to be the largest reported so far, the assumptions introduced in deriving equation 1 appear to be reasonable. Hence, the present result can be considered as the evidence for the high degree of ionicity in the binding of AgF.

However, in the case of Ag_2F, the situation is more complicated. According to X-ray measurements,[19] the silver atoms in Ag_2F crystals are in the position of iodine atoms in a CdI_2 lattice and are at the same distance from each other as prevails for the silver atoms in metallic silver. The fluorine atom occupies the Cd position in the lattice and the distance between the silver and fluorine atoms is the same as the interionic distance in normal silver fluoride. Thus, there must occur a reduction of the symmetry of the wave functions of fluorine in Ag_2F compared to that in AgF crystals, which is not taken into account in equation 1. If this equation were to be utilized as it stands, one would have to conclude from the resonance line shift of fluorine nucleus that Ag_2F is as covalent as CF_4 and ClF_3.



(a) AgF, 22 484_5 Mc. (b) Ag_2F, 22.488_2 Mc.

Fig. 2.—F^{19} resonance signals from AgF and Ag_2F with single 100 kc. markers.

There are three possible points of view with respect to this problem. First, the situation might be such that the excitation energy ΔE for Ag_2F is comparatively small, thus making the corresponding value of $\Delta\sigma$ less negative than the values of $\Delta\sigma$ for compounds with the same degree of ionic character in binding. Unfortunately, no information concerning the excitation energies of Ag_2F is available at present. Alternatively, the approximation used by Saika and Slichter in deriving equation 1 may be inapplicable to the present case, because of the modification of the meaning of the coefficient λ. As mentioned above, the value of $\left(\left\langle\frac{1}{r^3}\right\rangle_{\text{av}}\right)_{2\text{p}}$ in the Ag_2F lattice cannot be expressed correctly as the product $\lambda\left(\left\langle\frac{1}{r^3}\right\rangle_{\text{av}}\right)^0_{2\text{p}}$ as in the case of AgF. It can be expected that the effect of the reduction of symmetry of the electrostatic potential around the fluorine atom will make the value of $\left(\left\langle\frac{1}{r^3}\right\rangle_{\text{av}}\right)_{2\text{p}}$ smaller when the value of λ is the same. Hence, this effect does not seem to account for the greater paramagnetism in fluorine resonance of Ag_2F.

The third reason for the observed result may be found in the hyperfine interaction that is responsible for the Knight shift. Since Ag_2F is metallic in nature, such an effect can reasonably be anticipated. However, it will be smaller than the normally observed Knight shifts in metals, since the negative charge of the fluoride ion will make the probability of finding the conduction electrons at at the fluorine nucleus very small. The resonance line shift of Ag_2F, of 0.023% relative to AgF, is comparable to the smallest Knight shift observed in metals. This shift may well consist of both contributions, *i.e.*, the second order paramagnetism and the Knight shift.

The n.m.r. absorption signals shown in Figs. 1 and 2 are obtained by using about the same quantities of fluorides in the radiofrequency coil; thus, in the experiments with Ag_2F, the number of F^{19} nuclei in the coil was about half of that in the experiments with AgF. As mentioned previously, Ag_2F crystals dissipate an appreciable amount of the rf.

(19) Strukturberichte, Bd. I, 789; Bd. II, 276.

energy in the coil. Hence, it is expected that the Q value of the oscillator coil will be much smaller with Ag_2F samples than with AgF samples. Furthermore, the resonance signal from Ag_2F was obtained only at higher oscillation levels, because oscillation could not be sustained at lower levels. Nevertheless, the resonance signals from Ag_2F are of almost the same size as those from AgF. Consequently, the thermal relaxation time T_1 is expected to be much smaller in Ag_2F than in AgF. The decrease of T_1 values in Ag_2F could be attributed to the presence of defects. Actually, Hilsch, *et al.*,[10] suggested that the relatively large value of the residual resistivity of Ag_2F may be attributed to the presence of defects. The AgF sample used was extremely sensitive to the radiation in the visible region of the spectrum. In addition, it was prepared by a rapid precipitation process. As a consequence, the AgF sample must have had a large quantity of defects as well. In view of these facts, it seems natural to seek some other mechanisms that will explain the smaller T_1 value in Ag_2F. An explanation in terms of effects due to conduction electrons seems most plausible. As shown by Korringa,[20] the relaxation time T_1 is inversely proportional to the size of the Knight shift; *i.e.*, it is inversely proportional to the probability of finding conduction electrons at the nucleus. As mentioned above, this probability is expected to be rather small. Hence, the relaxation by the conduction electrons may not be the overwhelming contribution to T_1, even if the conduction electrons are really effective in reducing the T_1 value.

In the explanation of the result for Ag_2F, equation 1 cannot be utilized as such, because the simplifying assumptions on which equation 1 is based do not apply to this case. To obtain the appropriate theroretical expressions a study of Overhauser effect[13] and of the electrical resistivity perpendicular to the layers of Ag_2F as well as further T_1 measurements at different temperatures may be helpful.

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The Three Melting Points and Heats of Fusion of Phosgene. Entropy of Solids I and II, and Atomic Exchange Disorder in Solid II[1]

BY W. F. GIAUQUE AND J. B. OTT

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Carbonyl chloride has been found to have three melting points at 145.37, 142.09 and 139.19°K. for solids I, II and III, respectively. Solid I is the form with the stable melting point. The calorimetric heats of fusion of the three forms at their respective melting points are (I) 1371.5 ± 1, (II) 1335.4 ± 1.5 and (III) 1131 ± 5 cal. mole^{-1}. The heat capacity data of solid I were combined with calorimetric measurements of Giauque and Jones on the liquid and the heat of fusion and vaporization to obtain the entropy of the ideal gas at the boiling point, 280.71°K., as 66.99 gibbs mole^{-1} (the value at 298.15°K. = 67.81 gbs. mole^{-1}). These are in complete agreement with the values 66.99 and 67.81 gbs. mole^{-1} calculated from quantum statistics and molecular data for the above two temperatures. It has been shown that the previous heat capacity measurements on $COCl_2$ by Giauque and Jones apply to solid II rather than to solid I. The entropy of solid II at its melting point is shown to be 20.24 gbs. mole^{-1}; however, the $\int_0^T C_p \, d \ln T$ gives only 20.04. The discrepancy of 0.20 gbs. mole^{-1} is well beyond experimental error and is attributed to atomic exchange disorder frozen into the crystal. This amount of entropy corresponds to 1.75% of the molecules with oxygen and chlorine atoms in exchanged positions. The energy change accompanying this dislocation is calculated to be 1330 cal. mole^{-1} for the case of a small fraction of exchanged atoms. The thermodynamic properties of solid II are corrected for the effect of frozen in disorder and tables of thermodynamic properties are given for solids I, II, liquid and gaseous $COCl_2$. For a pressure of one atmosphere it may be calculated that solid III has no equilibrium transition to solid I. Similarly there is no transition point between solids II and III. Calculation indicates that solid II becomes the stable form below about 40°K. but there is a considerable margin of possible error in this result due to the very small difference in heat content between solids I and II.

The purpose of this paper is to clear up some discrepancies in the thermodynamics of carbonyl chloride, $COCl_2$. Giauque and Jones[2] carried out a low temperature calorimetric investigation which was used to calculate the entropy of carbonyl chloride gas at the boiling point. The value was found[3] to be 1.63 gbs. mole^{-1} less than the entropy calculated by utilizing fundamental frequencies of the molecule as given by Thompson.[4] Assuming the correctness of Thompson's values the entropy shortage in $\int C_p \, d \ln T$ was explainable as unexpected residual disorder in the solid at limiting low temperatures.

The experimental work of Giauque and Jones was rushed to completion in 1942 after they were engaged in war work and the haste left some unexplained occurrences which would normally have called for additional investigation. They comment on an expansion in the calorimeter, which strained the resistance thermometer over a region below the melting point and made it necessary to observe

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(1) This work was supported in part by the National Science Foundation.

(2) W. F. Giauque and W. M. Jones, THIS JOURNAL, **70**, 120 (1948).

(3) 1 gbs. (gibbs) = 1 defined cal./defined deg. K. See W. F. Giauque, E. W. Hornung, J. E. Kunzler and T. R. Rubin, *ibid.*, **82**, 62 (1960).

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