[CONTRIBUTION FROM CHEMISTRY DEPARTMENT, UNIVERSITY OF KENTUCKY]

Chloroform-bearing Chelates

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Vapor pressure–composition diagrams show that the acetylacetonates of iron, chromium and aluminum form with chloroform solvates which contain two moles of chloroform per mole of acetylacetonate. X-Ray powder patterns indicate that the solvates of iron, aluminum and chromium acetylacetonates have patterns which differ from those of the desolvated compounds. A structure in which the chloroform is sandwiched between the layers of the acetylacetonate crystals is proposed. The ability of an acetylacetonate to form a chloroformate apparently depends on its structure since tetrahedral, divalent metal chelates do not form crystalline chloroformates.

When iron(III) acetylacetonate is recrystallized from ethyl alcohol, diethyl ether or benzene, stable crystals of the unsolvated chelate are formed. In the course of preparing pure iron(III) acetylacetonate the crude product was dissolved in chloroform and filtered to remove any oxides which may have been present. When the chloroform solution was allowed to evaporate, large, red, crystalline prisms were obtained. On standing in air, however, these crystals apparently lost chloroform which was incorporated in the crystal and changed to orange-red, powdery pseudomorphs of the original crystals. Mention of chloroform solvates of iron acetylacetonate was made by Urbain and Debierne[1] but the compound was not characterized extensively. Chloroform-containing crystals also were obtained when aluminum(III) and chromium(III) acetylacetonates were recrystallized from chloroform. As long as the crystals were kept in a chloroform atmosphere they appeared to be stable, but they lost chloroform and became opaque within a half-hour when standing in air.

Only one other instance of chloroform bonded to a chelate was found in the literature.[2] Here it was postulated that two chloroform molecules were bonded along an axis normal to a planar cobalt complex.

Since it was difficult to imagine how chloroform was bonded to octahedral, trivalent metal acetylacetonates, and since non-aqueous solvates of metal chelates are relatively rare, it was decided to investigate more thoroughly the chloroform containing crystals of iron, aluminum and chromium acetylacetonates.

Experimental

Preparation of Chelates.—Ten grams of ferric ammonium sulfate was dissolved in 500 ml. of water saturated with acetylacetone. Ammonium hydroxide was added drop by drop until precipitation ceased. The crude iron acetylacetonate was filtered, dried and recrystallized twice from 95% ethyl alcohol to which a few ml. of acetylacetone had been added to prevent hydrolysis. The crystals were dried at 110° for two hours. Aluminum acetylacetonate was prepared in the same manner from aluminum nitrate from which traces of iron had been removed by extraction. Chromium acetylacetonate was prepared by treating potassium dichromate with a large excess of acetylacetone in water. As the chromate ion was reduced slowly by the acetylacetone, crystals of chromium(III) acetylacetonate formed. The crude crystals of chromium acetylacetonate were recrystallized twice from ethyl alcohol. Reagent grade chemicals were used throughout. The acetylacetonates were analyzed for the percentage of metal and in each case the theoretical and observed values coincided.

Measurement of Vapor Pressures.—The vapor pressure of chloroform above the mixed crystals was measured in an apparatus which consisted of a sample bulb, mercury manometer and a vacuum manifold. About one gram of the dry acetylacetonate was weighed into the sample bulb and mixed with glass helices which provided a surface area large enough to ensure rapid attainment of equilibrium. The helices also prevented bumping when the chloroform was removed. After the sample was weighed, the bulb was evacuated, closed off and removed from the system. Enough liquid chloroform to dissolve the sample was admitted and the bulb reweighed. The bulb was reattached, a small amount of chloroform removed, and the bulb was weighed. This process was repeated until all of the chloroform was removed; vapor pressure readings were taken at each step. The diagram which resulted is shown in Fig. 1. It is apparent that the vapor pressure in each instance dropped to a constant value when the mole ratio of chloroform to metal was exactly two. The rounding of the upper portion of the curves is caused by the 100 ml. of dead space between the sample and the manometer.

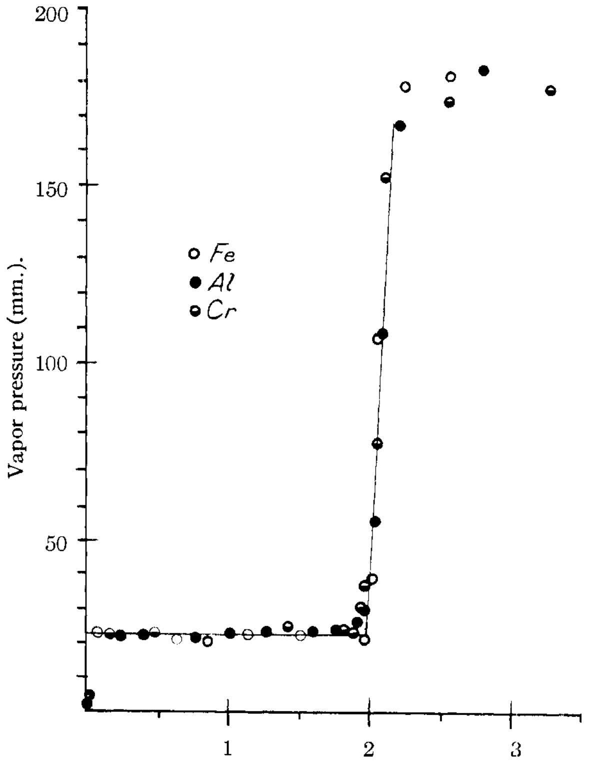

Fig. 1.—Vapor pressure-composition diagram.

All measurements for the vapor pressure diagram were made with the bulb immersed in a water-bath thermostated at 25 ± 0.05°. The variation with temperature of the vapor pressure above the mixed crystals (Fig. 3) was determined in the same apparatus with the bath thermostated at

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(1) G. Urbain and A. Debierne, *Compt. rend.*, **129**, 302 (1899).

(2) J. Endo, *J. Chem. Soc. Japan*, **65**, 34 (1955).

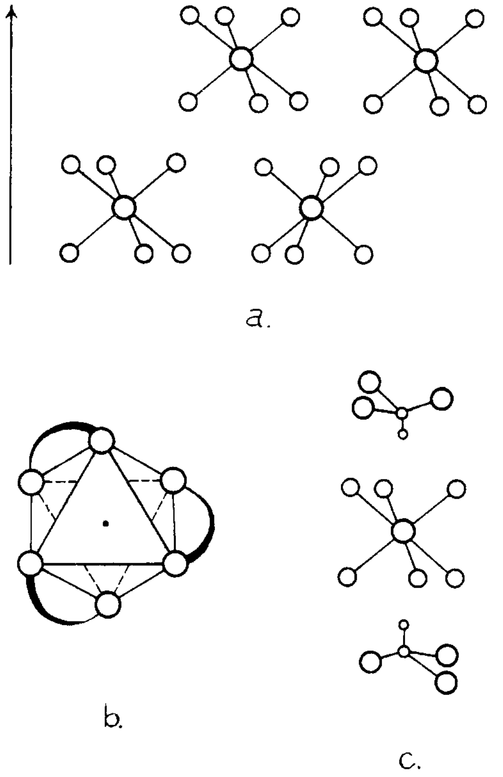

Fig. 2.—Structures of acetylacetonates (a and b) and chloroformate (c).

the indicated temperatures to within 0.05°. Identical vapor pressures were obtained whether the system was initially at either a higher or lower temperature than the final temperature. In all cases equilibrium was reached within a half-hour.

The X-ray powder patterns were taken in the usual manner. A sealed capillary was used to preserve the crystals containing chloroform.

Discussion

The graph showing vapor pressure as a function of composition (Fig. 1) indicates that compounds are formed between two moles of chloroform and one mole of either iron, aluminum or chromium acetylacetonate. Additional evidence of compound formation is found in the difference in X-ray diffraction patterns of the desolvated and solvated crystals (Table I).

Since compounds are formed, the question of how two chloroform molecules can be attached to octahedral complexes such as these must be considered. Willis and Mellor[3] have shown by a study of magnetic susceptibilities in various solvents that there seems to be a reaction between certain planar nickel complexes and basic solvents such as pyridine. In some cases the solvent is bonded directly to the metal, and the complexes are shifted from planar to octahedral. However, in compounds formed from chloroform and acetylacetonates, such an attachment is unlikely because formation of chloroform–metal bonds would require rupture of acetylacetonate–metal bonds if the metal is to retain its normal coördination number of six. Actually, this bond is little affected by the presence of the chloroform since the ultraviolet and visible spectra of the acetylacetonates in chloroform solutions are identical to those in benzene or alcohol.[4]

TABLE I

X-RAY DATA

$Fe(C_5H_7O_2)_3$		$Al(C_5H_7O_2)_3$		$Cr(C_5H_7O_2)_3$	
d (Å.)	*I*	*d* (Å.)	*I*	*d* (Å.)	*I*
8.27	s	8.16	vs	8.19	s
6.76	vs	6.93	s	6.96	m
(Broad)		6.65	vs	6.70	vs
5.23	m	5.32	m	5.37	m
4.35	vw	4.38	w	4.32	w
4.15	m	4.18	m	4.15	w
..		3.93	w	3.95	w
3.74	m	3.77	m	3.78	m
3.52	w	3.56	w	3.59	w
..		3.36	w	3.37	w
$Fe(C_5H_7O_2)_3 \cdot 2CHCl_3$		$Al(C_5H_7O_2)_3 \cdot 2\text{-}2CHCl_3$		$Cr(C_5H_7O_2)_3 \cdot 2CHCl_3$	
d (Å.)	*I*	*d* (Å.)	*I*	*d* (Å.)	*I*
10.7	w	..	..	10.4	w
7.51	vs	7.47	vs	7.47	vs
5.66	m	5.62	m	5.62	s
5.34	s	5.27	s	5.28	s
5.00	vvw	4.97	w	..	
4.42	vw	..		4.40	w
4.23	vw	..		4.20	w
3.89	m	..		..	
3.75	s	3.69	ms	3.69	s
3.54	m	3.48	w	3.54	m

A possible mode of arrangement for the additional chloroform molecules may be inferred from the structures of the chelates. Iron(III) acetylacetonate is the only trivalent acetylacetonate whose structure has been elucidated in detail,[5] although other acetylacetonates mentioned in this work are apparently similiar. In that determination the octahedral character of the iron(III) acetylacetonate was confirmed, and the structure found to consist of discrete molecules in layers perpendicular to the *b*-axis of the orthorhombic unit cell and held together by van der Waals forces. The layer nature of the structure is shown schematically by the octahedra of Fig. 2a. There is at least a formal similarity between this structure and that of the layer-lattice silicate minerals. Moreover, iron(III) acetylacetonate shows a pronounced cleavage on 010. The layer character of these chelates and the ease of separation of the layers suggests that the chloroform molecules may be taken up between the layers of the crystals, resulting in an expansion of the *b*-axis. It is possible that the hydrogen atom of the chloroform is attracted to the oxygens of the acetylacetonate in view of the evidence for the formation of hydrogen bonds between chloroform and carbonyl oxygens.[6,7]

The molecule of iron(III) acetylacetonate possesses only one threefold inversion axis which is shown piercing the center of the molecule in Fig. 2b. If the two chloroform molecules were bonded along this axis above and below the chelate molecule (Fig. 2c) a solvate with the highest possible

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[3] J. B. Willis and D. P. Mellor, THIS JOURNAL, **69**, 1237 (1947).

[4] W. N. McNerney, unpublished data, University of Kentucky.

[5] R. B. Roof, *Acta Cryst.*, **9**, 781 (1956).

[6] W. Klemperer, M. W. Cronyn, A. H. Maki and G. C. Pimentel, THIS JOURNAL, **76**, 5846 (1954).

[7] C. M. Huggins, G. C. Pimentel and J. N. Shoolery, *J. Chem. Phys.*, **23**, 1244 (1955).

symmetry would be formed. The X-ray powder method used here is not sufficiently powerful to provide the final answer to the question of chloroform attachment, but there is an indication that a lattice expansion has occurred, causing the appearance of weak lines at 10.4–10.6 Å. in at least two of the patterns. Unfortunately, the symmetry of the crystals is too low to allow unequivocal indexing of more than a few lines.

It is not probable that a hydrogen bond is formed between the chlorine of chloroform and the methylene hydrogen of the acetylacetonate since carbon tetrachloride shows no tendency to form similar solvates. If, as seems likely, the positions assumed by the chloroform molecules are these shown in Fig. 2c, the hydrogen would be linked to three oxygen atoms, and the result could be called a "trifurcated hydrogen bond." There are objections[8] to calling such a conformation a hydrogen bond since the bonds are not linear. Possibly there is a hydrogen bond formed to only one of the three oxygens at random throughout the structure, or perhaps there is a simple electrostatic attraction between the chloroform dipole and the oxygens.

An attempt was made to find a value for the energy of bond formation in these compounds. A plot of the vapor pressure as a function of temperature is shown in Fig. 3. From the slope of the lines and the van't Hoff equation, a value of ΔH^0 of approximately 13 kcal./mole was calculated for the reaction

$$M(C_5H_7O_2)_3 \cdot 2CHCl_3 \rightleftarrows 2CHCl_3 + M(C_5H_7O_2)_3$$

where M is either iron, aluminum or chromium. This value is equivalent to an energy of approximately 6 kcal. for each chloroform–metal bond. Since the heat of decomposition of the compound (per chloroform–chelate bond) is no greater than the heat of vaporization of chloroform, the bonding must be due largely to van der Waals forces. If a hydrogen bond exists it must be a very weak one.

The tetrahedral copper, zinc and cadmium acetylacetonates do not form crystalline solvates with chloroform. This seems to indicate that the spacing of the oxygens is of major significance in the formation of solvates of this type. It also should be noted that in general the solubility of the trivalent acetylacetonates in chloroform is much higher than that of the divalent acetylacetonates.

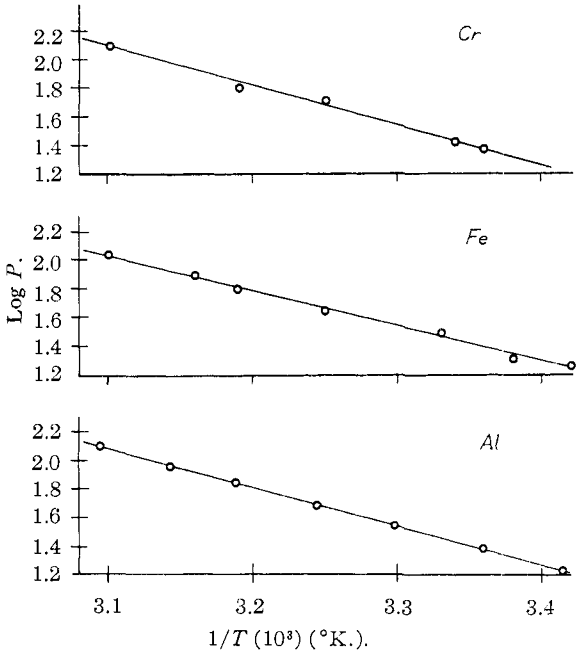

Fig. 3.—Vapor pressure of chloroformates as a function of ($1/T$).

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[8] J. Donohue, *J. Phys. Chem.*, **56**, 502 (1952).

[CONTRIBUTION NO. 2237 FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY]

Shock Waves in Chemical Kinetics: The Decomposition of N_2O_5 at High Temperatures[1]

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The shock pyrolysis of N_2O_5 in the presence of excess argon has been studied, thus providing information about the properties and reactions of the nitrate free radical, NO_3. The important reactions are: $N_2O_5 \rightleftarrows NO_2 + NO_3$ (A and B), $NO_2 + NO_3 \rightarrow NO + O_2 + NO_2$ (e), $NO + NO_3 \rightarrow 2NO_2$ (f), $NO_3 + NO_3 \rightarrow 2NO_2 + O_2$ (g). In the concentration and temperature range studied ([argon] ~ 0.0076 mole/l., 450–550°K.), the dissociation reaction is a unimolecular reaction close to its second order low pressure limit, $-\,d[N_2O_5]/dt = A'[A][N_2O_5]$, with $A' = 10^{13.7}\exp(-16{,}500 \pm 700/RT)$(mole/l.)$^{-1}$ sec.$^{-1}$. The equilibrium constant of the dissociation reaction is given by $K_c = 10^{4.97}\exp(-20{,}100 \pm 1100/RT)$(mole/l.). The rate constants of e and g are given (550–1100°K.) by $e = 2.3 \times 10^8\exp(-4400 \pm 700/RT)$(mole/l.)$^{-1}$ sec.$^{-1}$ and $g = 2.6 \times 10^9$ $\exp(-7700 \pm 1000/RT)$(mole/l.)$^{-1}$ sec.$^{-1}$. On the basis of this and other data, the following thermodynamic quantities are calculated: $N_2O_5 = NO_2 + NO_3$, $\Delta H^0_{300°K.} = 21{,}600$ cal./mole, $\Delta S^0_{300°K.} = 33.6$ e.u., $\Delta H^0_{f,300}(NO_3) = 17{,}100\ (\pm 1000)$ cal./mole, $S^0_{300}(NO_3) = 60 \pm 2$ e.u. The kinetics of various reactions involving NO_3 are reviewed and recommended rate constants and activation energies at 300°K. computed. In general, the present investigation, where NO_3 was a major constituent whose concentration was directly measured, confirms the results of previous investigations in which NO_3 was present at low, undetermined concentrations as a reactive intermediate.

(1) Research carried out under contract Nonr-220(01) between the Office of Naval Research and the California Institute of Technology. This paper was presented to the 130th National Meeting, American Chemical Society, Atlantic City, N. J., September, 1956. A more detailed account is contained in the Ph.D. thesis of Garry L. Schott, California Institute of Technology, 1956.