density and molecular weight measurements. However, crude measurements with a Monel Bourdon gauge, as well as the behavior of $FC(O)ONF_2$ during vacuum line manipulations, suggested a normal boiling point in the vicinity of 0°.

Caution! Although no explosions occurred during the course of this work, the materials are potentially hazardous and proper shielding should be used.

Acknowledgments.—The authors thank Dr. B. B. Stewart for the nmr spectra, Mr. E. McCarthy for the mass spectroscopic results, and Miss R. Juurik for the chemical analyses. This research was supported by the Advanced Research Projects Agency, Propellant Chemistry Office, and was monitored by Army Research Missile Command, Redstone Arsenal, Huntsville, Ala., under Contracts DA-30-069-ORD-2638 and DA-01-021-AMC-12264(Z).

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Reactions of Gallium Alkoxides with Acyl Halides

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Received February 1, 1967

Halide alkoxides of a number of elements (*e.g.*, Ti,[1] Zr,[2] Al,[3] Fe,[4] and V[5]) have been synthesized by the reactions of their alkoxides with acyl halides. In a recent communication Mogele[6] has reported the preparation of halide alkoxides of gallium by reactions of the type

$$Ga(GaX_4) + 2ROH \longrightarrow XGa(OR)_2 + GaX_3 + H_2$$

$$GaX_3 + 2NaOR \longrightarrow XGa(OR)_2 + 2NaX$$

where $X = Cl$ or Br and $R = CH_3$ or C_2H_5. These monohalide derivatives were found to be insoluble in organic solvents and were assumed to be coordinatively polymeric. Dihalide monoalkoxy derivatives could not be prepared by similar reactions, since the dihalide derivatives initially formed were found to yield the monohalide derivatives. The dihalide derivatives could finally be prepared by reactions of the type

$$XGa(OR)_2 + GaX_3 \longrightarrow 2X_2GaOR$$

$$X_2GaR + ROH \longrightarrow X_2GaOR + RH$$

where $X = Cl$ or Br and $R = CH_3$ or C_2H_5.

TABLE I

INFRARED BANDS OF THE COMPOUNDS[a]

Compound	Bands, cm^{-1}														
$Ga(i\text{-}C_3H_7O)_2Cl$ (distld)[b,c]	...	...	3580 w	...	...	...	3025 s	2965 s (A)	...	2905 s	...	...	...		
$Ga(i\text{-}C_3H_7O)Cl_2$ (distld)[b,d]	3700 vw	3645 w	3610 vw	...	3100 s	3080 s (A)	3040 s	2985 s (A)	...	2915 s	2890 w (B)	2830 vw	2660 w		
$GaCl_3\cdot i\text{-}C_3H_7OOCCH_3$[b,d]	3700 w	3650 w	3600 vw	3445 vw	3090 s	3070 s (A)	3035 s	2980 s (A)	2940 sh	...	2895 w (B)	2815 w	2655 w		
$Ga(i\text{-}C_3H_7O)_2Cl$	...	2375 m	...	...	...	...	...	...	...	...	...	...	1500 s	1445 m (D)	1395 s (D)
$Ga(i\text{-}C_3H_7O)Cl_2$	2605 w	2370 w	2330 w	2210 w	2010 w	1960 m	1810 s	1755 w	...	1670 w	1615 w	1580 w	1520 w	1465 s (D)	1385 m (D)
$GaCl_3\cdot i\text{-}C_3H_7OOCCH_3$	2600 w	...	2315 w	2205 w	2000 vw	1955 m	1805 s	...	1705 w (C)	...	1605 w	1580 w	1515 w	1460 m (D)	...
$Ga(i\text{-}C_3H_7O)_2Cl$	1365 m (D)	1295 s	...	...	1218 s, b	...	1155 w (E)	1122 w	1064 vw	1028 w	942 m				
$Ga(i\text{-}C_3H_7O)Cl_2$	...	...	...	1245 w	...	1173 w (E)	1140 s (E)	1117 w	...	1035 s	945 m (E)				
$GaCl_3\cdot i\text{-}C_3H_7OOCCH_3$	1360 s (D)	...	1254 s	1250 sh	...	1180 m (E)	1145 m (E)	1107 s	...	1032 s	957 m (E)				
$Ga(i\text{-}C_3H_7O)_2Cl$	933 s	883 w	843 w	...	753 s, b	665 s	615 w (F)	593 w (F)	...						
$Ga(i\text{-}(C_3H_7O)Cl_2$	925 w	...	843 w	814 w (E)	768 w	668 s, b	610 sh (F)	...	...						
$GaCl_3\cdot i\text{-}C_3H_7OOCCH_3$	...	885 w	845 w	815 w (E)	768 w	670 s, b	620 sh (F)	605 m (F)	422 w (F)						

[a] s = strong, m = medium, w = weak, vw = very weak, b = broad, sh = shoulder. [b] Most of the unclassified peaks may be assigned to the solvent used. [c] Solvent: chloroform. [d] Solvent: benzene.

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In view of the unstable character and difficulties in handling gallium mono- and trihalides, it was thought worthwhile to attempt the synthesis of halide alkoxides by the reaction of gallium alkoxides with acyl halides. In our work the reactions of gallium isopropoxide with acetyl chloride and bromide have been found to proceed smoothly yielding the mono-, di-, and trihalide products quantitatively according to the stoichiometric ratio of the reactants taken. These reactions, therefore, can be represented by the equations

$$(i\text{-}C_3H_7O)_3Ga + CH_3COX \longrightarrow (i\text{-}C_3H_7O)_2GaX + i\text{-}C_3H_7OOCCH_3$$

$$(i\text{-}C_3H_7O)_3Ga + 2CH_3COX \longrightarrow (i\text{-}C_3H_7O)GaX_2 + 2(i\text{-}C_3H_7OOCCH_3)$$

$$(i\text{-}C_3H_7O)_3Ga + 3CH_3COX \longrightarrow GaX_3\cdot i\text{-}C_3H_7OOCCH_3 + 2(i\text{-}C_3H_7OOCCH_3)$$

where X = Cl or Br.

All the halide–isopropoxide derivatives, $(i\text{-}C_3H_7O)_2GaX$ and $i\text{-}C_3H_7OGaX_2$, were found to be soluble in common organic solvents. Ebullioscopic determination of molecular weights indicated their trimeric and dimeric nature, respectively, in boiling benzene and also in carbon tetrachloride. The molecular weights observed in both the solvents did not show any noticeable concentration effect. As a typical example the molecular weights of $Ga(i\text{-}C_3H_7O)_2Cl$ at concentrations (represented by weights of solutes in grams in 15 ml of benzene) given in parentheses are: 685 (0.1574), 693 (0.3038), 681 (0.3588), 690 (0.4317), 693 (0.5477).

The addition compounds, $GaX_3\cdot i\text{-}C_3H_7OOCCH_3$, formed with excess acyl halides were also soluble in benzene and carbon tetrachloride in which they showed dimeric behavior. On being heated under reduced pressure the products began to decompose at about 150° leaving a reddish residue out of which no gallium chloride could be volatilized.

The ready formation of single products from different stoichiometric ratios of the gallium isopropoxide and acyl halides appeared to indicate a facile group interchangeability; this was confirmed by the reaction of gallium isopropoxide with 2 mol of gallium chloride, when the following interchange appears to take place

$$(i\text{-}C_3H_7O)_3Ga + 2GaCl_3 \longrightarrow 3i\text{-}C_3H_7OGaX_2$$

For comparison, a reaction of gallium ethoxide with acetyl chloride in 1:2 molar ratio was carried out and was found to yield $Ga(OC_2H_5)Cl_2$

$$Ga(OC_2H_5)_3 + 2CH_3COCl \longrightarrow Ga(OC_2H_5)Cl_2 + 2C_2H_5OOCCH_3$$

The product was found to be soluble in benzene in which it showed a dimeric behavior.

Infrared spectra of the chloro derivatives have been recorded in the range 4000–400 cm^{-1} and the following modes have been assigned on the basis of previous measurements:[7,8] (A) ν(C—H), (B) $\nu(CH_3)$, (C) ν(C=O), (D) $\delta(CH_3)$, (E) ν skeletal $\text{—CH}<\begin{smallmatrix}CH_3\\ CH_3\end{smallmatrix}$, and (F) ν (Ga—O). The data are given in Table I.

Experimental Section

The reactions were carried out in all-glass apparatus with interchangeable joints. Extreme care was taken to exclude moisture during all of the experiments.

Gallium isopropoxide was prepared by the reaction of gallium chloride with sodium isopropoxide as already described[9] and purified by distillation under reduced pressure. Benzene (BDH) was dried over sodium wire and finally distilled azeotropically with ethanol over a column. Acetyl halides (BDH) were fractionated carefully before use.

TABLE II

REACTIONS OF GALLIUM ISOPROPOXIDE WITH ACYL HALIDES

Wt of $(i\text{-}(C_3H_7O)_3$-Ga, g	Wt of acyl halide, g (molar ratio)	Compound formed (wt, g)	State	Bp, °C (mm)	Analysis of the distilled product, %						Mol wt in			
					Gallium		Halide		Alkoxy		C_6H_6		CCl_4	
					Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
1.673	0.539 (1:1)	$(i\text{-}C_3H_7O)_2GaCl$ (1.514)	Colorless solid	110 (0.4)	31.12	31.15	15.91	15.85	52.86	51.84	223	681	223	660
2.436	1.554 (1:2)	$(i\text{-}C_3H_7O)GaCl_2$ (1.970)	Colorless liquid	60 (0.4)	34.90	34.30	35.55	35.30	29.54	29.07	200	428	200	393
1.875	1.801 (1:3)	$GaCl_3\cdot i\text{-}C_3H_7OOCCH_3$ (2.117)	Brown liquid	150 (0.4)[a]	25.06	24.89[b]	38.29	38.08[b]	...	... [b]	278	573	278	554
2.246	1.123 (1:1)	$(i\text{-}C_3H_7O)_2GaBr$ (2.436)	Colorless solid	118 (1.0)	26.05	26.14	29.85	29.96	...	...	268	776	268	757
2.230	2.225 (1:2)	$(i\text{-}C_3H_7O)GaBr_2$ (2.608)	Colorless liquid	92 (1.0)	24.15	24.47	55.39	55.47	...	...	289	622	289	586
1.452	2.173 (1:3)	$GaBr_3\cdot i\text{-}C_3H_7OOCCH_3$ (2.422)	Orange liquid	170 (0.4)[a]	16.94	16.85[b]	58.28	57.62[b]	...	... [b]	411	785	411	816
	$GaCl_3$													
1.399	2.00 (1:2)	$(i\text{-}C_3H_7O)GaCl_2$ (3.396)	Colorless liquid	76 (2.5)	34.90	34.80	35.55	35.68	29.54	30.19	200	418	...	...
$Ga(OC_2H_5)_3$	CH_3COCl													
1.700	1.325 (1:2)	$Ga(OC_2H_5)Cl_2$ (1.542)	Colorless liquid	76 (1.5)	37.54	37.42	38.23	38.06	24.23	24.01	186	372	...	...

[a] Decomposed. [b] These analyses are for the undistilled products.

Gallium and halides were estimated as the oxinate and as silver halides, respectively. Isopropoxy and ethoxy contents were determined by an oxidimetric method.[10]

Molecular weights were determined in a semimicro ebul-

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liometer (Gallenkamp) using a thermistor sensing in boiling benzene and carbon tetrachloride.

Synthetic Reactions. Reaction of Gallium Isopropoxide with Acetyl Chloride in Molar Ratio 1:1.—Acetyl chloride (0.54 g) was added in two or three lots to a solution of gallium isopropoxide (1.67 g) in dry benzene (20 g). An exothermic reaction took place. The mixture was refluxed for 2 hr at a bath temperature of 90–100°. On cooling, nothing appeared to crystallize. The excess benzene was therefore distilled out under reduced pressure. Finally a white solid (1.51 g, yield 100%) was obtained by drying the product for 3 hr at 0.1 mm pressure at room temperature (25°). *Anal.* Calcd for $Ga(i\text{-}C_3H_7O)_2Cl$: Ga, 31.23; Cl, 15.91; $i\text{-}C_3H_7O$, 52.86. Found: Ga, 31.18; Cl, 15.87; $i\text{-}C_3H_7O$, 52.1.

The compound (0.41 g) was distilled at 110° (0.4 mm) to give a colorless liquid (0.28 g) which solidified after a few minutes. *Anal.* Found: Ga, 31.15; Cl, 15.85; $i\text{-}C_3H_7O$, 51.84. The melting point of this compound is 74.75°. The analogous bromo derivative melts at 95–96°.

The general method of synthesis was the same in every case; hence the other derivatives are described in Table II.

Acknowledgments. S. R. B. is grateful to the C.S.I.R., New Delhi, for the award of a Junior Research Fellowship. The authors' thanks are due to Dr. V. K. Mathur for discussion of the infrared spectra.

CONTRIBUTION FROM ROCKETDYNE, A DIVISION OF NORTH
AMERICAN AVIATION, INC., CANOGA PARK, CALIFORNIA

Difluoramine: Reactions with Chlorine Fluorides

BY D. PILIPOVICH AND C. J. SCHACK

Received March 20, 1967

The action of chlorine fluorides on organic compounds has been reviewed with respect to the more quantitative aspects of chlorofluorination and the degree of competition between the chlorination and fluorination processes.[1] Since difluoramine is a readily oxidized compound[2] we were interested in studying the system HNF_2–ClF_x in order to determine whether general halogenation occurred and to what extent competition existed between the chlorination and the fluorination processes.

Experimental Section

Materials.—Chlorine monofluoride was prepared by heating an equimolar mixture of chlorine and fluorine to 150° for several hours in a stainless steel cylinder. The product was purified by vacuum fractionation prior to use. Chlorine trifluoride was purchased from the Matheson Co. and purified by the method of Schack, *et al.*[3] Chlorine pentafluoride was prepared by the method of Pilipovich, *et al.*,[4] which involved the fluorination of $CsClF_4$. Chlorine fluorides of high purity were essential. Freedom from chlorine oxides was most important since such impurities often caused the reactions with difluoramine to occur with an explosive deflagration. Difluoramine was generated from difluorourea as reported by Lawton, *et al.*[5] Alkali fluorides were fused and then powdered in a drybox prior to use.

Apparatus.—Difluoramine was handled in a glass vacuum line and the chlorine fluorides in a stainless steel vacuum line fitted with Teflon U traps. Because difluoramine is decomposed by fluorine-passivated metal and the chlorine fluorides are difficult to manipulate in glass, the reactions of these materials were conducted in a Kel-F cylinder fitted with a Teflon valve. Reaction products were separated on the metal system.

Infrared spectra were taken on a Perkin-Elmer Infracord 137 using 5-cm Kel-F or stainless steel cells fitted with AgCl windows. Mixtures of chlorodifluoramine and tetrafluorohydrazine were not separable by fractional condensation and the relative proportions of such mixtures were determined by infrared absorbance measurements. Pure samples of $ClNF_2$ and N_2F_4 were employed to obtain the necessary coefficients. The experimental values are: $ClNF_2$, $a_{845\text{cm}^{-1}} = 7.2 \times 10^{-3}$ mm^{-1} cm^{-1} and $a_{685\text{cm}^{-1}} = 4.4 \times 10^{-3}$ mm^{-1} cm^{-1}; N_2F_4, $a_{735\text{cm}^{-1}} = 2.3 \times 10^{-3}$ mm^{-1} cm^{-1}. Errors in the analysis are probably on the order to 5% including the errors of gas volume measurements.

Reaction of ClF and HNF_2.—After pretreating the Kel-F reactor with ClF_3, it was evacuated and attached to the glass vacuum line. Difluoramine (32.1 cm^3, 1.43 mmol) was condensed into the reactor at −142°. The closed reactor was reattached to the metal vacuum line and ClF was condensed in at −142°, the quantity (32.0 cm^3, 1.43 mmol) being measured by pressure difference since ClF has a low vapor pressure at this temperature. After 30 min at −78°, the product gases were separated by fractional condensation at −142 and −196°. The high-temperature fraction was found to be HF without any infrared-observable contaminants. The low-temperature sample (31.9 cm^3) did not contain any unreacted ClF, but was composed of a mixture of 97% $ClNF_2$ and 3% N_2F_4. The latter may have arisen through incomplete reaction of the difluoramine and its subsequent decomposition in the metal line during fractionation[6] or through decomposition of $ClNF_2$ to N_2F_4 and Cl_2 as reported by Petry.[7]

Reaction of ClF_3 and HNF_2.—Chlorine trifluoride (8.1 cm^3, 0 362 mmol) was condensed into the Kel-F reactor at −196°. The valve was closed and the reactor connected to the glass line from which HNF_2 (24.2 cm^3, 1.07 mmol) was obtained by condensation at −142°. The reactor was then immersed in a bath cooled to −78°. After 30 min, the reactor was opened and the products were fractionated on the metal vacuum system. An infrared spectrum of the material trapped at −142° showed no Cl–F or N–F species but only HF. Similar inspection of the −196° condensate (16.2 cm^3) revealed a 1:1 mixture of N_2F_4 and $ClNF_2$ with less than 1% NF_3. Replicate measurements showed 7.8 and 8.4 cm^3 of $ClNF_2$ to be present in addition to 8.1 cm^3 of N_2F_4. Thus the reaction was complete and nearly quantitative in a 1:3 ratio of ClF_3 to HNF_2. Several experiments were carried out with lesser amounts of either reactant. In these cases the reaction ratio of 1:3 was still observed and the excess reactant was recovered.

Reaction of ClF_5 and HNF_2.—A sample of ClF_5 (37.6 cm^3, 1.68 mmol) was condensed into the reactor at −142° followed by HNF_2 (38.9 cm^3, 1.73 mmol). The closed reactor was warmed to −78° for 10 min before fractionation of the products was initiated. Some noncondensable gas was produced but not measured. Most of the ClF_5 was recovered unreacted (28.4 cm^3). No HNF_2 was recovered but 9.2 cm^3 of $ClNF_2$, 15.1 cm^3 of N_2F_4, and a trace of NF_3 were obtained along with 39 ml of HF. Thus, somewhat over 4 HNF_2 reacted for each ClF_5 producing 1 $ClNF_2$ and somewhat less than 2 N_2F_4.

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