

TABLE II  
FUNDAMENTAL VIBRATIONS OF DIPHOSPHINE

Schematic description	Solid			Vapor <sup>d</sup>		
	C <sub>2h</sub> species	No.	Cm <sup>-1</sup>	C <sub>s</sub> species	No.	Cm <sup>-1</sup>
PH str	a <sub>g</sub>	1	2281 <sup>a</sup>	a	2	2312
PH <sub>2</sub> scissors		2	1049		3	e
PH <sub>2</sub> wag		3	(653) <sup>b</sup>		5	743
PP str		4	437		6	e
PH str	a <sub>u</sub>	5	2296 <sup>a</sup>	1	2312	
PH <sub>2</sub> twist		6	781	4	792	
PH <sub>2</sub> rock (torsion)		7	(169) <sup>c</sup>	7	e	
PH str	b <sub>g</sub>	8	2281 <sup>a</sup>	b	9	2312
PH <sub>2</sub> twist		9	878	11	827	
PH str	b <sub>u</sub>	10	2296 <sup>a</sup>	8	2312	
PH <sub>2</sub> scissors		11	1053 <sup>a</sup>	10	1081	
PH <sub>2</sub> wag		12	636 <sup>a</sup>	12	633	

<sup>a</sup> Mean of doublet. <sup>b</sup> From liquid diphosphine.<sup>2,3</sup> <sup>c</sup> Possible impurity band. <sup>d</sup> Wave numbers from ref 1. <sup>e</sup> Not reported.

tings in diphosphine are not unreasonable. Further evidence suggesting that the Raman doublet 1056 and 1043 cm<sup>-1</sup> can be attributed to fg splitting is that only one band (1070 cm<sup>-1</sup>) was reported in this region in the Raman spectrum of the liquid.<sup>2</sup> We tentatively attribute the doublets near 2200 cm<sup>-1</sup> to fg splitting, although they may well arise from separate molecular fundamentals.

The 878-cm<sup>-1</sup> Raman band in the solid shifts to 856 cm<sup>-1</sup> in the liquid,<sup>2</sup> and it appears to correlate with the 827-cm<sup>-1</sup> infrared band in the gas. It therefore appears that the three bands originate from a similar fundamental, which provides strong evidence that the effective symmetry of P<sub>2</sub>H<sub>4</sub> in the gas is lower than C<sub>2h</sub>. The large gas-solid shift of this band, with the solid at higher frequency, supports the possibility of a *gauche-trans* change of structure on condensation.

A vibrational assignment of the solid on the basis of C<sub>2h</sub> symmetry is given in Table I, and fundamentals of the solid and vapor are tentatively summarized in Table II. The deformation fundamentals are assigned by analogy with the well-established fundamentals of N<sub>2</sub>H<sub>4</sub>,<sup>9</sup> so that their frequencies decrease along the series: PH<sub>2</sub> scissors > PH<sub>2</sub> twist > PH<sub>2</sub> wag. This results in different assignments of  $\nu_3$ ,  $\nu_6$ , and  $\nu_{12}$  in the solid from those proposed by Nixon,<sup>1</sup> which do not appear compatible with the *trans* structure in the solid. The assignment of 169 cm<sup>-1</sup> to the torsion  $\nu_7$  is somewhat uncertain since Baudler and Schmidt have reported the presence of an impurity band near here in the Raman spectrum of the liquid.<sup>2,3</sup>

In conclusion, it is interesting to note that *trans* structures have been proposed for P<sub>2</sub>H<sub>4</sub>(s), P<sub>2</sub>I<sub>4</sub>,<sup>7,10</sup> P<sub>2</sub>Cl<sub>4</sub>,<sup>6</sup> and P<sub>2</sub>F<sub>4</sub>,<sup>11</sup> in contrast to the *gauche* structures reported for P<sub>2</sub>H<sub>4</sub>(g)<sup>1</sup> and N<sub>2</sub>H<sub>4</sub>,<sup>12,13</sup> while N<sub>2</sub>F<sub>4</sub> has been reported to consist of both *trans* and *gauche* isomers.<sup>14</sup>

**Acknowledgment.**—I am grateful to Dr. G. L. Carlson and Mr. F. E. Kiviat for recording the Raman spectrum, and to Professor F. A. Miller for his interest in this work. The work was supported by the U. S. Army Research Office, Durham, N. C., under Grant ARO-D-31-124-G-735. I gratefully acknowledge an ICI Research Fellowship at University College, London, England.

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### On the Preparation of Perchloryl Fluoride by Acid Solvolysis of Perchlorates in Fluorinated Solvents

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Perchloryl fluoride, ClO<sub>3</sub>F, has been prepared by the action of elemental fluorine on potassium perchlorate,<sup>1</sup> by the electrolysis of sodium perchlorate in anhydrous hydrofluoric acid,<sup>2</sup> and by reactions of various metal perchlorates with fluorinated Lewis acid-solvent systems (HSO<sub>3</sub>F,<sup>3</sup> SbF<sub>5</sub>,<sup>4</sup> or mixtures thereof<sup>4</sup>). Although the Lewis acid-perchlorate processes for ClO<sub>3</sub>F synthesis are claimed in the patent literature,<sup>3,4</sup> details of the technique are insufficient to test the validity of the mechanism advanced by Woolf to explain the reaction of perchlorates with fluorosulfonic acid. The present study, in which the ClO<sub>3</sub>F yields and reaction temperatures were shown to correlate with Lewis acid strength of the medium, suggests an underlying mechanism involving solvolysis similar to that proposed by Woolf.

#### Experimental Section

Solutions of KClO<sub>4</sub> in anhydrous HF were prepared in tubes made of polychlorotrifluoroethylene closed with Swagelok-fitted Teflon valves for connection to a Monel Metal vacuum line. Weighed quantities of the anhydrous perchlorate salt were transferred into the tube in a plastic dry bag under an atmosphere of dry nitrogen. Anhydrous HF was distilled into the tube and the resulting solution then treated with an excess of AsF<sub>5</sub>, SbF<sub>5</sub>, or BF<sub>3</sub> condensed into the tube at -196°. The reaction mixture was warmed slowly to 20° and samples of vapor were withdrawn successively into a gas infrared cell (Monel Metal with AgCl windows) connected into a section of the vacuum manifold of known volume. No attempts were made in this study to isolate the ClO<sub>3</sub>F produced; instead, yields were based on measurements of the vapors above the reaction mixture. The spectra of the vapors from the reaction mixtures containing AsF<sub>5</sub> and SbF<sub>5</sub> showed only ClO<sub>3</sub>F and HF. These vapors could easily be separated, if desired, by passage

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TABLE I  
SUMMARY OF DATA FROM PERCHLORATE SOLVOLYSIS  
EXPERIMENTS IN VARIOUS MEDIA

Source of ClO <sub>4</sub> <sup>-</sup>	Re-action medium	Lewis acid added	Min temp at which ClO <sub>3</sub> F first detected, °C	High-est reaction temp, °C	ClO <sub>4</sub> <sup>-</sup> used, mmol	ClO <sub>3</sub> F recovered, mmol	% yield of ClO <sub>3</sub> F based on ClO <sub>4</sub> <sup>-</sup>
KClO <sub>4</sub>	HF	AsF <sub>5</sub>	-20	20	0.48	0.42	87
KClO <sub>4</sub>	HF	SbF <sub>5</sub>	-40	20	0.48	>0.34 <sup>a</sup>	>70 <sup>a</sup>
KClO <sub>4</sub>	HF	SbF <sub>5</sub>	-40	20	1.11	1.02	92
KClO <sub>4</sub>	HF	BF <sub>3</sub>	...	35	0.48	None	0
KClO <sub>4</sub>	AsF <sub>5</sub>	AsF <sub>5</sub>	-5	25	0.52	0.35	67
CsClO <sub>4</sub>	IF <sub>5</sub>	AsF <sub>5</sub>	0	25	0.22	0.18	82
CsClO <sub>4</sub>	IF <sub>5</sub>	SbF <sub>5</sub>	0	25	0.25	0.22	88
CsClO <sub>4</sub>	BrF <sub>5</sub>	AsF <sub>5</sub>	-30	25	0.076	0.060	80

<sup>a</sup> All ClO<sub>3</sub>F generated was not recovered.

through a column of NaF whereby pure ClO<sub>3</sub>F would be obtained. The yield of ClO<sub>3</sub>F was estimated from the infrared absorption band at 9.4 μ by reference to a calibration curve relating absorbance to pressure. In a typical experiment, a total of 190 mm of ClO<sub>3</sub>F in a 40-cc volume (0.42 mmol) was collected from 0.065 g of KClO<sub>4</sub> (0.48 mmol) in 0.6 ml of HF treated with 18 cc of AsF<sub>5</sub>(g) (0.75 mmol) corresponding to a yield of 87%.

No ClO<sub>3</sub>F was detected when a solution of KClO<sub>4</sub> in HF was treated with BF<sub>3</sub> under similar conditions. In this case, a large proportion of the BF<sub>3</sub> was recovered in the vapor samples withdrawn for infrared examination, leaving unreacted KClO<sub>4</sub> in HF solution as the final residue. The residual reaction mixtures from the systems containing AsF<sub>5</sub> or SbF<sub>5</sub> consisted of suspensions of KAsF<sub>6</sub> or KSbF<sub>6</sub> in HF, respectively.

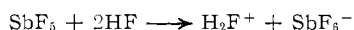
Similar reactions were carried out with KClO<sub>4</sub> or CsClO<sub>4</sub> in other media such as AsF<sub>5</sub>, IF<sub>5</sub>, and BrF<sub>5</sub>, using AsF<sub>5</sub> or SbF<sub>5</sub>. The experimental procedures were similar to those employed in the systems containing HF and are based on conventional vacuum line transfer techniques.

A summary of the data obtained is presented in Table I.

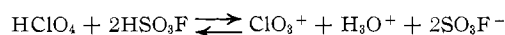
### Discussion

Since the Lewis acids AsF<sub>5</sub> and SbF<sub>5</sub> are believed to increase the concentration of solvent cation in the solvents HF,<sup>5</sup> AsF<sub>5</sub>,<sup>6</sup> and IF<sub>5</sub>,<sup>7</sup> the process whereby these substances promote the formation of ClO<sub>3</sub>F from ClO<sub>4</sub><sup>-</sup> probably involves acid solvolysis.

Thus, the interaction of SbF<sub>5</sub> with anhydrous HF leads to a highly acidic system containing H<sub>2</sub>F<sup>+</sup>



On the basis of conductance and boiling point elevation data, Fredenhagen<sup>8</sup> concluded that solutions of KClO<sub>4</sub> in anhydrous HF contain ClO<sub>4</sub><sup>-</sup> ions in equilibrium with the protonated species H<sub>2</sub>ClO<sub>4</sub><sup>+</sup>. The latter species is derived from the solvolysis of KClO<sub>4</sub> to HClO<sub>4</sub> and subsequent protonation of the latter by the strongly acid solvent, HF. The concentration of protonated species would be expected to increase in the presence of the even more highly acidic system which results upon addition of SbF<sub>5</sub>. This is consistent with Woolf's postulation<sup>9</sup> that HClO<sub>4</sub> dissociates in fluosulfonic acid as a base



although this mode of dissociation of perchlorates in fluosulfonic acid is not consistent with recent conductance data.<sup>10</sup> The protonated species H<sub>2</sub>ClO<sub>4</sub><sup>+</sup> may be considered as a hydrated form of ClO<sub>3</sub><sup>+</sup>, analogous to the more firmly established species H<sub>2</sub>NO<sub>3</sub><sup>+</sup> in HF solutions of nitrates. The chemical reactivities of the latter solutions are consistent with the presence of NO<sub>2</sub><sup>+</sup> (e.g., the nitration of benzene to nitrobenzene by KNO<sub>3</sub> in HF).

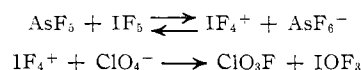
Accordingly, the production of ClO<sub>3</sub>F by Lewis-acid-promoted solvolysis of perchlorates may proceed by one of the following reaction mechanisms.

(a) The first is the formation of an intermediate ion-pair complex of the form H<sub>2</sub>F<sup>+</sup>ClO<sub>4</sub><sup>-</sup> which decomposes into H<sub>2</sub>O and ClO<sub>3</sub>F. A Lewis acid such as AsF<sub>5</sub> or SbF<sub>5</sub> may promote the reaction by increasing the concentration of the species H<sub>2</sub>F<sup>+</sup> or by attacking an oxygen of the basic ClO<sub>4</sub><sup>-</sup> moiety. The latter interaction would be more likely to involve the free Lewis acid than the fluoride-coordinated species (i.e., SbF<sub>5</sub> rather than SbF<sub>6</sub><sup>-</sup>). Although the major fraction of the antimony in a solution of  $\frac{1}{2}$ SbF<sub>5</sub> in HF is in the form of SbF<sub>6</sub><sup>-</sup>, some SbF<sub>5</sub> may also be present in the equilibrium.<sup>11</sup> In pure HF, the concentration of the ionic species H<sub>2</sub>F<sup>+</sup> is extremely low, as indicated by the auto-ionization constant 10<sup>-10</sup>.<sup>12</sup> Hence, formation of ClO<sub>3</sub>F proceeds to an insignificant extent in HF solutions of alkali perchlorates in the absence of additives which increase H<sub>2</sub>F<sup>+</sup>.

(b) The second is the formation of an intermediate ion-pair complex of the form ClO<sub>3</sub><sup>+</sup>SbF<sub>6</sub><sup>-</sup> which, unlike ClO<sub>2</sub><sup>+</sup>SbF<sub>6</sub><sup>-</sup>,<sup>13</sup> may be unstable and yield ClO<sub>3</sub>F and SbF<sub>5</sub> on dissociation. Thus, preliminary studies indicate that the solvolysis of the chlorate KClO<sub>3</sub> in IF<sub>5</sub>, promoted by AsF<sub>5</sub>, yields ClO<sub>2</sub><sup>+</sup>AsF<sub>6</sub><sup>-</sup> which remains in the solution phase and requires treatment with excess KF to liberate chloryl fluoride, ClO<sub>2</sub>F. An interesting reaction supporting the existence, at least as a transitory species, of ClO<sub>3</sub><sup>+</sup> is the production of perchlorylbenzene from ClO<sub>3</sub>F and benzene in the presence of AlCl<sub>3</sub> by a Friedel-Crafts type of reaction.<sup>14</sup>

Establishment of the fate of the fourth oxygen atom of the ClO<sub>4</sub><sup>-</sup> during the reaction would clarify the reaction mechanism.

A similar mechanism can be invoked to explain the Lewis-acid-promoted solvolysis of perchlorates in other media such as AsF<sub>5</sub>, IF<sub>5</sub>, or BrF<sub>5</sub>. Thus



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The example cited is quite analogous to the reaction of  $\text{KMnO}_4$  and  $\text{IF}_5$  which yields  $\text{MnO}_3\text{F} + \text{IOF}_3$ .<sup>15</sup> The isolation of  $\text{IOF}_3$  or compounds with an  $\text{Sb}-\text{O}$  bond from the perchlorate solvolysis reaction mixture would aid in elucidating the reaction mechanism.

The inability of  $\text{BF}_3$  to promote the solvolysis of perchlorate in an  $\text{HF}$  medium confirms that  $\text{BF}_3$  is not a strong acid in  $\text{HF}$ .<sup>16</sup> Acid strengths in  $\text{HF}$  decrease in the order  $\text{SbF}_5 > \text{PF}_5 > \text{BF}_3$ ,<sup>5,16</sup> which is consistent with the slightly higher yields and lower reaction temperature observed for  $\text{SbF}_5$  in comparison with  $\text{AsF}_5$  (Table I).

**Acknowledgment.**—This research was supported by the Advanced Research Projects Agency, Propellant Chemistry Office, and was monitored by the Army Research Missile Command, Redstone Arsenal, Huntsville, Ala., under Contract No. DA-30-069-ORD-2638.

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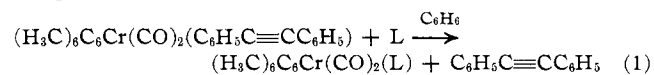
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## Kinetic and Synthetic Studies of Olefin and Acetylene Complexes of Hexamethylbenzenetricarbonylchromium

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Recent kinetic studies indicate that the reactions of  $\text{C}_6\text{H}_5\text{Mn}(\text{CO})_2(\text{olefin})$  with phosphines,  $\text{L}$ , to form  $\text{C}_6\text{H}_5\text{Mn}(\text{CO})_2(\text{L})$  proceed by way of an  $\text{S}_{\text{N}}1$  mechanism.<sup>1</sup> The rates of reaction vary greatly with the nature of the olefin. In an attempt to understand the behavior of olefins in similar compounds, we prepared several complexes of the type  $(\text{H}_3\text{C})_6\text{C}_6\text{Cr}(\text{CO})_2(\text{olefin})$ . Since it had previously been reported<sup>2</sup> that some of these complexes reacted with  $\text{P}(\text{C}_6\text{H}_5)_3$  to form  $(\text{H}_3\text{C})_6\text{C}_6\text{Cr}(\text{CO})_2\text{P}(\text{C}_6\text{H}_5)_3$ , we planned to examine the kinetics of these reactions. For reasons of instability, insolubility, or unreactivity, however, it was possible to study extensively only the reaction of  $(\text{H}_3\text{C})_6\text{C}_6\text{Cr}(\text{CO})_2(\text{C}_6\text{H}_5\text{C}\equiv\text{CC}_6\text{H}_5)$  with several nucleophiles



In this paper, we report the synthesis of several  $(\text{H}_3\text{C})_6\text{C}_6\text{Cr}(\text{CO})_2(\text{olefin})$  derivatives and the results of the kinetic study of reaction 1.

### Experimental Section

**Preparation and Purification of Materials.**— $(\text{H}_3\text{C})_6\text{C}_6\text{Cr}(\text{CO})_3$ <sup>3</sup> and  $(\text{H}_3\text{C})_6\text{C}_6\text{Cr}(\text{CO})_2(\text{C}_6\text{H}_5\text{C}\equiv\text{CC}_6\text{H}_5)$ <sup>2</sup> were prepared using

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procedures reported in the literature. Reagent grade  $\text{P}(\text{C}_6\text{H}_5)_3$ ,  $\text{P}(\text{OC}_6\text{H}_5)_3$ , and  $\text{As}(\text{C}_6\text{H}_5)_3$  were not purified further. The  $\text{P}(n\text{-C}_4\text{H}_9)_3$  was purified by fractional distillation at reduced pressure. Tetrahydrofuran (THF) was distilled from  $\text{LiAlH}_4$  immediately before use. Reagent grade benzene was saturated with  $\text{N}_2$  before using.

The  $(\text{H}_3\text{C})_6\text{C}_6\text{Cr}(\text{CO})_2(\text{olefin})$  complexes were prepared by irradiating in a quartz tube a solution, under a nitrogen atmosphere, of 40 ml of THF containing 0.005 mol of  $(\text{H}_3\text{C})_6\text{C}_6\text{Cr}(\text{CO})_3$  and a slight excess of the desired olefin for 4–5 hr with a Hanovia ultraviolet lamp. Details of isolation and characterization of the complexes from the irradiated solutions are given below.

**$(\text{H}_3\text{C})_6\text{C}_6\text{Cr}(\text{CO})_2(\text{maleic acid})$ .**—The red THF solution was concentrated to 20 ml under a water-aspirator vacuum. After filtration, the resulting crystals were washed with benzene to remove unreacted  $(\text{H}_3\text{C})_6\text{C}_6\text{Cr}(\text{CO})_3$  and then with  $\text{CH}_3\text{OH}$  to remove excess maleic acid. The yield of the red-orange crystals was 0.96 g (49%).

*Anal.* Calcd for  $(\text{H}_3\text{C})_6\text{C}_6\text{Cr}(\text{CO})_2(\text{C}_4\text{H}_4\text{O}_4)$ : C, 55.95; H, 5.75. Found: C, 55.85; H, 5.81. The compound decomposes at 143–145° and is stable in air for several weeks.

**$(\text{H}_3\text{C})_6\text{C}_6\text{Cr}(\text{CO})_2(\text{fumaric acid})$ .**—This compound was isolated in the same manner as for the maleic acid complex. Owing to the instability of the complex, all operations must be carried out in a nitrogen atmosphere. The yield was 43%.

*Anal.* Calcd for  $(\text{H}_3\text{C})_6\text{C}_6\text{Cr}(\text{CO})_2(\text{C}_4\text{H}_4\text{O}_4)$ : C, 55.95; H, 5.75. Found: C, 55.65; H, 5.76. The complex decomposes at 133–135°, and its solutions decompose rapidly in air.

**$(\text{H}_3\text{C})_6\text{C}_6\text{Cr}(\text{CO})_2(\text{endic anhydride})$ .**—The irradiated solution was filtered and evaporated to dryness under vacuum. The resulting yellow-orange crystals were dissolved in 25 ml of benzene, leaving unreacted endic anhydride (*endo-cis*-bicyclo-[2.2.1]-5-heptene-2,3-dicarboxylic anhydride). After filtration, the solution was evaporated to 15 ml, and the product (73% yield) precipitated upon adding 25 ml of heptane.

*Anal.* Calcd for  $(\text{H}_3\text{C})_6\text{C}_6\text{Cr}(\text{CO})_2(\text{C}_9\text{H}_8\text{O}_3)$ : C, 63.58; H, 6.03. Found: C, 61.45; H, 5.98. The compound decomposes at 123–125° and in air slowly at room temperature.

Other complexes— $(\text{H}_3\text{C})_6\text{C}_6\text{Cr}(\text{CO})_2(\text{maleic anhydride})$ ,  $(\text{H}_3\text{C})_6\text{C}_6\text{Cr}(\text{CO})_2(\text{citraconic anhydride})$ , and  $(\text{H}_3\text{C})_6\text{C}_6\text{Cr}(\text{CO})_2(\text{H}_3\text{CO}_2\text{CC}\equiv\text{CCO}_2\text{CH}_3)$ —were prepared similarly and identified only by their characteristic infrared spectra (Table I).

TABLE I  
C–O STRETCHING FREQUENCIES OF  
 $(\text{H}_3\text{C})_6\text{C}_6\text{Cr}(\text{CO})_2(\text{olefin})$

Olefin	Solvent	C–O str, $\text{cm}^{-1}$	
Cyclopentene	Benzene	1883	1835 <sup>a</sup>
Endic anhydride	Benzene	1902	1838
$\text{C}_6\text{H}_5\text{C}\equiv\text{CC}_6\text{H}_5$	Benzene	1912	1835 <sup>a</sup>
Fumaric acid	KBr	1933	1861
Maleic acid	KBr	1924	1870
Citraconic anhydride	$\text{CHCl}_3$	1959	1893
Maleic anhydride	$\text{CHCl}_3$	1967	1906

<sup>a</sup> Reference 2.

**Determination of Rates of Reaction.**—Freshly prepared benzene solutions of  $(\text{H}_3\text{C})_6\text{C}_6\text{Cr}(\text{CO})_2(\text{C}_6\text{H}_5\text{C}\equiv\text{CC}_6\text{H}_5)$ ,  $\sim 1 \times 10^{-3} M$ , and of the ligand  $\text{L}$  were placed separately under  $\text{N}_2$  in a two-leg reaction flask fitted with a serum cap. Since laboratory light causes considerable decomposition of the complex, the reaction vessel was carefully wrapped with aluminum foil. After thermostating the vessel at the desired temperature ( $\pm 0.05^\circ$ ) for about 15 min, the reaction was started by tilting and mixing the solutions in the two legs of the vessel. At appropriate time intervals, a sample was withdrawn with a syringe and the absorbance of the solution at 500  $\mu\text{m}$  was determined on a Cary 14 ultraviolet-visible spectrophotometer. At this wavelength the reactant absorbs quite strongly whereas the extinction coefficients for the products,  $(\text{H}_3\text{C})_6\text{C}_6\text{Cr}(\text{CO})_2(\text{L})$ , are