TABLE II

FUNDAMENTAL VIBRATIONS OF DIPHOSPHINE

Schematic description	Solid: C_{2h} species	Solid: No.	Solid: Cm^{-1}	Vapor[d]: C_2 species	Vapor[d]: No.	Vapor[d]: Cm^{-1}
PH str	a_g	1	2281[a]	a	2	2312
PH_2 scissors		2	1049		3	*e*
PH_2 wag		3	(653)[b]		5	743
PP str		4	437		6	*e*
PH str	a_u	5	2296[a]		1	2312
PH_2 twist		6	781		4	792
PH_2 rock (torsion)		7	(169)[c]		7	*e*
PH str	b_g	8	2281[a]	b	9	2312
PH_2 twist		9	878		11	827
PH str	b_u	10	2296[a]		8	2312
PH_2 scissors		11	1053[a]		10	1081
PH_2 wag		12	636[a]		12	633

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

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

The 878-cm^{-1} Raman band in the solid shifts to 856 cm^{-1} in the liquid,[2] and it appears to correlate with the 827-cm^{-1} 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_2H_4 in the gas is lower than C_{2h}. 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_{2h} 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_2H_4,[9] so that their frequencies decrease along the series: PH_2 scissors > PH_2 twist > PH_2 wag. This results in different assignments of ν_3, ν_6, and ν_{12} in the solid from those proposed by Nixon,[1] which do not appear compatible with the *trans* structure in the solid. The assignment of 169 cm^{-1} to the torsion ν_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.[2,3]

In conclusion, it is interesting to note that *trans* structures have been proposed for $P_2H_4(s)$, P_2I_4,[7,10] P_2Cl_4,[6] and P_2F_4,[11] in contrast to the *gauche* structures reported for $P_2H_4(g)$[1] and N_2H_4,[12,13] while N_2F_4 has been reported to consist of both *trans* and *gauche* isomers.[14]

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[9] A. Yamaguchi, *Nippon Kagaku Zasshi*, **80**, 1109 (1959).

[10] Y. C. Leung and J. Waser, *J. Phys. Chem.*, **60**, 539 (1956).

[11] R. W. Rudolph, R. C. Taylor, and R. W. Parry, *J. Am. Chem. Soc.*, **88**, 3729 (1966).

[12] A. Yamaguchi, I. Ichishima, T. Shimanouchi, and S-I. Mizushima, *Spectrochim. Acta*, **16**, 1471 (1960).

[13] T. Kasuya, and T. Kojima, *J. Phys. Soc. Japan*, **18**, 364 (1963); *Sci. Papers Inst. Phys. Chem. Res.* (Tokyo), **56**, 1 (1956).

[14] D. F. Koster and F. A. Miller, *Spectrochim. Acta*, in press.

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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_3F, has been prepared by the action of elemental fluorine on potassium perchlorate,[1] by the electrolysis of sodium perchlorate in anhydrous hydrofluoric acid,[2] and by reactions of various metal perchlorates with fluorinated Lewis acid–solvent systems (HSO_3F,[3] SbF_5,[4] or mixtures thereof[4]). Although the Lewis acid–perchlorate processes for ClO_3F synthesis are claimed in the patent literature,[3,4] 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_3F 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 $KClO_4$ 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_5, SbF_5, or BF_3 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_3F 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_5 and SbF_5 showed only ClO_3F and HF. These vapors could easily be separated, if desired, by passage

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[1] H. Bode and E. Klesper, *Z. Anorg. Allgem. Chem.*, **266**, 275 (1951).

[2] A. Englebrecht and H. Atzwanger, *Monatsh.*, **83**, 1087 (1952); *J. Inorg. Nucl. Chem.*, **2**, 348 (1956).

[3] G. Barth-Wehrenalp, *ibid.*, **2**, 266 (1956); U. S. Patent 2,942,948 (June 28, 1960); W. A. LaLande, Jr., U. S. Patent 2,982,617 (May 2, 1961).

[4] G. Barth-Wehrenalp and H. C. Mandell, Jr., U. S. Patent 2,942,949 (June 28, 1960).

TABLE I

SUMMARY OF DATA FROM PERCHLORATE SOLVOLYSIS EXPERIMENTS IN VARIOUS MEDIA

Source of ClO_4^-	Reaction medium	Lewis acid added	Min temp at which ClO_3F first detected, °C	Highest reaction temp, °C	ClO_4^- used, mmol	ClO_3F recovered, mmol	% yield of ClO_3F based on ClO_4^-
$KClO_4$	HF	AsF_5	−20	20	0.48	0.42	87
$KClO_4$	HF	SbF_5	−40	20	0.48	>0.34[a]	>70[a]
$KClO_4$	HF	SbF_5	−40	20	1.11	1.02	92
$KClO_4$	HF	BF_3	...	35	0.48	None	0
$KClO_4$	AsF_3	AsF_5	−5	25	0.52	0.35	67
$CsClO_4$	IF_5	AsF_5	0	25	0.22	0.18	82
$CsClO_4$	IF_5	SbF_5	0	25	0.25	0.22	88
$CsClO_4$	BrF_5	AsF_5	−30	25	0.076	0.060	80

[a] All ClO_3F generated was not recovered.

through a column of NaF whereby pure ClO_3F would be obtained. The yield of ClO_3F 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_3F in a 40-cc volume (0.42 mmol) was collected from 0.065 g of $KClO_4$ (0.48 mmol) in 0.6 ml of HF treated with 18 cc of $AsF_5(g)$ (0.75 mmol) corresponding to a yield of 87%.

No ClO_3F was detected when a solution of $KClO_4$ in HF was treated with BF_3 under similar conditions. In this case, a large proportion of the BF_3 was recovered in the vapor samples withdrawn for infrared examination, leaving unreacted $KClO_4$ in HF solution as the final residue. The residual reaction mixtures from the systems containing AsF_5 or SbF_5 consisted of suspensions of $KAsF_6$ or $KSbF_6$ in HF, respectively.

Similar reactions were carried out with $KClO_4$ or $CsClO_4$ in other media such as AsF_3, IF_5, and BrF_5, using AsF_5 or SbF_5. 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_5 and SbF_5 are believed to increase the concentration of solvent cation in the solvents HF,[5] AsF_3,[6] and IF_5,[7] the process whereby these substances promote the formation of ClO_3F from ClO_4^- probably involves acid solvolysis.

Thus, the interaction of SbF_5 with anhydrous HF leads to a highly acidic system containing H_2F^+

$$SbF_5 + 2HF \longrightarrow H_2F^+ + SbF_6^-$$

On the basis of conductance and boiling point elevation data, Fredenhagen[8] concluded that solutions of $KClO_4$ in anhydrous HF contain ClO_4^- ions in equilibrium with the protonated species $H_2ClO_4^+$. The latter species is derived from the solvolysis of $KClO_4$ to $HClO_4$ 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_5. This is consistent with Woolf's postulation[9] that $HClO_4$ dissociates in fluosulfonic acid as a base

$$HClO_4 + 2HSO_3F \rightleftarrows ClO_3^+ + H_3O^+ + 2SO_3F^-$$

although this mode of dissociation of perchlorates in fluosulfonic acid is not consistent with recent conductance data.[10] The protonated species $H_2ClO_4^+$ may be considered as a hydrated form of ClO_3^+, analogous to the more firmly established species $H_2NO_3^+$ in HF solutions of nitrates. The chemical reactivities of the latter solutions are consistent with the presence of NO_2^+ (*e.g.*, the nitration of benzene to nitrobenzene by KNO_3 in HF).

Accordingly, the production of ClO_3F 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 $H_2F^+ClO_4^-$ which decomposes into H_2O and ClO_3F. A Lewis acid such as AsF_5 or SbF_5 may promote the reaction by increasing the concentration of the species H_2F^+ or by attacking an oxygen of the basic ClO_4^- moiety. The latter interaction would be more likely to involve the free Lewis acid than the fluoride-coordinated species (*i.e.*, SbF_5 rather than SbF_6^-). Although the major fraction of the antimony in a solution of SbF_5 in HF is in the form of SbF_6^-, some SbF_5 may also be present in the equilibrium.[11] In pure HF, the concentration of the ionic species H_2F^+ is extremely low, as indicated by the autoionization constant 10^{-10}.[12] Hence, formation of ClO_3F proceeds to an insignificant extent in HF solutions of alkali perchlorates in the absence of additives which increase H_2F^+.

(b) The second is the formation of an intermediate ion-pair complex of the form $ClO_3^+SbF_6^-$ which, unlike $ClO_2^+SbF_6^-$,[13] may be unstable and yield ClO_3F and SbF_5 on dissociation. Thus, preliminary studies indicate that the solvolysis of the chlorate $KClO_3$ in IF_5, promoted by AsF_5, yields $ClO_2^+AsF_6^-$ which remains in the solution phase and requires treatment with excess KF to liberate chloryl fluoride, ClO_2F. An interesting reaction supporting the existence, at least as a transitory species, of ClO_3^+ is the production of perchlorylbenzene from ClO_3F and benzene in the presence of $AlCl_3$ by a Friedel–Crafts type of reaction.[14]

Establishment of the fate of the fourth oxygen atom of the ClO_4^- 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_3, IF_5, or BrF_5. Thus

$$AsF_5 + IF_5 \rightleftarrows IF_4^+ + AsF_6^-$$

$$IF_4^+ + ClO_4^- \longrightarrow ClO_3F + IOF_3$$

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(5) A. F. Clifford, Ph.D. Thesis, University of Delaware, 1949.

(6) A. A. Woolf and N. N. Greenwood, *J. Chem. Soc.*, 2200 (1950).

(7) A. A. Woolf, *ibid.*, 3678 (1950).

(8) K. Fredenhagen and H. Fredenhagen, *Z. Anorg. Allgem. Chem.*, **243**, 39 (1939).

(9) A. A. Woolf, *J. Inorg. Nucl. Chem.*, **3**, 250 (1956).

(10) J. Barr, R. J. Gillespie, and R. C. Thompson, *Inorg. Chem.*, **3**, 1149 (1964).

(11) H. H. Hyman, L. A. Quarterman, M. Kilpatrick, and J. J. Katz, *J. Phys. Chem.*, **65**, 123 (1961).

(12) M. Kilpatrick and F. E. Luborsky, *J. Am. Chem. Soc.*, **76**, 5865 (1954).

(13) A. A. Woolf, *J. Chem. Soc.*, 4113 (1954).

(14) C. E. Inman, R. E. Oesterling, and E. A. Tyczkowski, *J. Am. Chem. Soc.*, **80**, 5286 (1958).

The example cited is quite analogous to the reaction of $KMnO_4$ and IF_5 which yields $MnO_3F + IOF_3$.[15] The isolation of IOF_3 or compounds with an Sb–O bond from the perchlorate solvolysis reaction mixture would aid in elucidating the reaction mechanism.

The inability of BF_3 to promote the solvolysis of perchlorate in an HF medium confirms that BF_3 is not a strong acid in HF.[16] Acid strengths in HF decrease in the order $SbF_5 > PF_5 > BF_3$,[5,16] which is consistent with the slightly higher yields and lower reaction temperature observed for SbF_5 in comparison with AsF_5 (Table I).

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(15) E. E. Aynsley, *J. Chem. Soc.*, 2425 (1958).

(16) A. F. Clifford and S. Kongpricha, *J. Inorg. Nucl. Chem.*, **20**, 147 (1961).

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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 $C_5H_5Mn(CO)_2$(olefin) with phosphines, L, to form $C_5H_5Mn(CO)_2(L)$ proceed by way of an SN1 mechanism.[1] 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 $(H_3C)_6C_6Cr(CO)_2$(olefin). Since it had previously been reported[2] that some of these complexes reacted with $P(C_6H_5)_3$ to form $(H_3C)_6C_6Cr(CO)_2P(C_6H_5)_3$, 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 $(H_3C)_6C_6Cr(CO)_2(C_6H_5C{\equiv}CC_6H_5)$ with several nucleophiles

$$(H_3C)_6C_6Cr(CO)_2(C_6H_5C{\equiv}CC_6H_5) + L \xrightarrow{C_6H_6} (H_3C)_6C_6Cr(CO)_2(L) + C_6H_5C{\equiv}CC_6H_5 \quad (1)$$

In this paper, we report the synthesis of several $(H_3C)_6C_6Cr(CO)_2$(olefin) derivatives and the results of the kinetic study of reaction 1.

Experimental Section

Preparation and Purification of Materials.—$(H_3C)_6C_6Cr(CO)_3$[3] and $(H_3C)_6C_6Cr(CO)_2(C_6H_5C{\equiv}CC_6H_5)$[2] were prepared using procedures reported in the literature. Reagent grade $P(C_6H_5)_3$, $P(OC_6H_5)_3$, and $As(C_6H_5)_3$ were not purified further. The $P(n\text{-}C_4H_9)_3$ was purified by fractional distillation at reduced pressure. Tetrahydrofuran (THF) was distilled from $LiAlH_4$ immediately before use. Reagent grade benzene was saturated with N_2 before using.

The $(H_3C)_6C_6Cr(CO)_2$(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 $(H_3C)_6C_6Cr(CO)_3$ 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.

$(H_3C)_6C_6Cr(CO)_2$(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 $(H_3C)_6C_6Cr(CO)_3$ and then with CH_3OH to remove excess maleic acid. The yield of the red-orange crystals was 0.96 g (49%).

Anal. Calcd for $(H_3C)_6C_6Cr(CO)_2(C_4H_4O_4)$: 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.

$(H_3C)_6C_6Cr(CO)_2$(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 $(H_3C)_6C_6Cr(CO)_2(C_4H_4O_4)$: 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.

$(H_3C)_6C_6Cr(CO)_2$(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 $(H_3C)_6C_6Cr(CO)_2(C_9H_8O_3)$: 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—$(H_3C)_6C_6Cr(CO)_2$(maleic anhydride), $(H_3C)_6C_6Cr(CO)_2$(citraconic anhydride), and $(H_3C)_6C_6Cr(CO)_2(H_3CO_2CC{\equiv}CCO_2CH_3)$—were prepared similarly and identified only by their characteristic infrared spectra (Table I).

TABLE I
C–O STRETCHING FREQUENCIES OF $(H_3C)_6C_6Cr(CO)_2$(olefin)

Olefin	Solvent	C–O str, cm^{-1}	
Cyclopentene	Benzene	1883	1835[a]
Endic anhydride	Benzene	1902	1838
$C_6H_5C{\equiv}CC_6H_5$	Benzene	1912	1835[a]
Fumaric acid	KBr	1933	1861
Maleic acid	KBr	1924	1870
Citraconic anhydride	$CHCl_3$	1959	1893
Maleic anhydride	$CHCl_3$	1967	1906

[a] Reference 2.

Determination of Rates of Reaction.—Freshly prepared benzene solutions of $(H_3C)_6C_6Cr(CO)_2(C_6H_5C{\equiv}CC_6H_5)$, $\sim 1 \times 10^{-3}$ *M*, and of the ligand L were placed separately under 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 (±0.05°) 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 mμ was determined on a Cary 14 ultraviolet–visible spectrophotometer. At this wavelength the reactant absorbs quite strongly whereas the extinction coefficients for the products, $(H_3C)_6C_6Cr(CO)_2(L)$, are

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(1) R. J. Angelici and W. Loewen, *Inorg. Chem.*, **6**, 682 (1967).

(2) W. Strohmeier and H. Hellmann, *Chem. Ber.*, **98**, 1598 (1965).

(3) B. Nicholls and M. C. Whiting, *J. Chem. Soc.*, 551 (1959).