Anal. Calcd. for C_3F_8O (diluted with 55.0% N_2): C, 7.9; F, 33.5. Found: C, 8.2; F, 33.0.

Identification of $(CF_3)_2CFOF$ was on the basis of n.m.r. and infrared spectra, elemental analysis, thermal decomposition products, and the reductive defluorination reaction.

Preparation of 2-Fluoroxyperfluoro-2-methylpropane. Perfluoro-*t*-butyl alcohol was kindly supplied by Dr. F. J. Pavlik of our Chemical Division Laboratories. Fluorination of 0.87 g. (3.7 mmoles) of this compound was carried out over a 5-hr. period at −20° with 0.12 mole of fluorine (5% in nitrogen). The collection trap was found to contain 1.7 mmoles, consisting principally (>95%) of $(CF_3)_3COF$. 2-Fluoroxyperfluoro-2-methylpropane was purified by gas chromatography at 0°. Elemental analyses of chromatographed $(CF_3)_3COF$ are shown below. The molecular weight of this material was found to be 252 (calcd., 254).

Anal. Calcd. for $C_4F_{10}O$: C, 18.9; F, 74.8. Found: C, 18.9; F, 74.4.

Identification of $(CF_3)_3COF$ was on the basis of n.m.r. and infrared spectra, elemental analysis, molecular weight, oxidizing power, thermal decomposition products, and other chemical reactions.

Preparation of 1-Nitro-2-fluoroxyperfluoroethane. A 3-g. (14 mmoles) sample of 1,1,1-trichloro-3-nitro-2-propanol (K & K Laboratories, Inc.) was treated with 1.3 moles of fluorine at 20° under the following conditions: 4%, 2.5 hr.; 11%, 1.5 hr.; 25%, 1.5 hr.; 41%, 2.5 hr. The contents of the collection trap were fractionated at reduced pressure through traps at −78, −111, and −196°. 1-Nitro-2-fluoroxyperfluoroethane was found in both the −78 and −111° fractions. The yield of this material was approximately 5%. The −78° fraction was also found to contain 1,1-dichloro-2-fluoroxyperfluoroethane and 1,1,1-trichloro-2-fluoroxyperfluoroethane.

Identification of $O_2NCF_2CF_2OF$ was on the basis of n.m.r. and infrared spectra and thermal decomposition products. Identifications of Cl_2CFCF_2OF and Cl_3CCF_2OF were on the basis of n.m.r. spectra and thermal decomposition products.

Preparation of 1-Chloro-2-fluoroxyperfluoroethane. A 2-g. (13 mmoles) sample of 2,2,2-trichloroethanol (Columbia Organic Chemicals Co., Inc.) was treated with 0.3 mole of fluorine at a concentration of 40% at −20° for 3.0 hr. and then at 20° for 2.0 hr. The contents of the collection trap were fractionated at reduced pressure through traps at −78, −111, and −196°. The medium boiling fraction was found to contain $ClCF_2CF_2OF$ in less than 2% yield. The high boiling fraction was found to contain Cl_2CFCF_2OF in approximately 5% yield. 1-Chloro-2-fluoroxyperfluoroethane was purified by gas chromatography at 0°. Its retention time was 70 relative to trichlorofluoromethane. Elemental analysis was carried out on a sample of chromatographed $ClCF_2CF_2OF$.

Anal. Calcd. for C_2F_5OCl: C, 14.1; F, 55.7. Found: C, 14.0; F, 56.0.

Identification of $ClCF_2CF_2OF$ was on the basis of n.m.r. and infrared spectra, elemental analysis, and thermal decomposition products.

The Quantitative Synthesis and Dimethylamine Reaction of Tris(trifluoromethyl)phosphine Oxide[1]

Anton B. Burg and Adib J. Sarkis

Contribution from the Department of Chemistry, University of Southern California, Los Angeles, California 90007. Received September 16, 1964

The phosphine $(CF_3)_3P$ with NO_2 quantitatively forms NO and the oxide $(CF_3)_3PO$ (m.p. −89°; b.p. 32°), which with $(CH_3)_2NH$ quantitatively forms HCF_3 and the new phosphinic amide $(CF_3)_2P(O)N(CH_3)_2$ (m.p. −21°; b.p. 154.6° estd.). This reversibly forms a solid 1:1 BF_3 adduct, the dissociation pressures of which give $\Delta F = 27.42 − 0.07257T$ kcal. The amide can be converted by excess pressure of HCl to $(CF_3)_2P(O)Cl$ (over 98%), thus offering a convenient route to other fluorocarbonphosphinyl chemistry. Accurate infrared spectra are reported for $(CF_3)_3PO$, $(CF_3)_2P(O)N(CH_3)_2$, and $(CF_3)_2P(O)Cl$.

The phosphine oxide $(CF_3)_3PO$ was first made, in yields approaching 70%, by the reaction of $(CF_3)_3PCl_2$ with oxalic acid.[2] We have found that it can be made quantitatively by a reaction occurring well below room temperature, namely
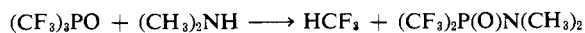
$$(CF_3)_3P + NO_2 \longrightarrow (CF_3)_3PO + NO$$

The value of this phosphine oxide for further syntheses

(2) R. C. Paul, *J. Chem. Soc.*, 574 (1955).

is illustrated by its quantitative reaction with dimethylamine

$$(CF_3)_3PO + (CH_3)_2NH \longrightarrow HCF_3 + (CF_3)_2P(O)N(CH_3)_2$$

also complete below room temperature. Then with a high enough pressure of dry hydrogen chloride the reaction

$$(CF_3)_2P(O)N(CH_3)_2 + 2HCl \longrightarrow (CH_3)_2NH_2Cl + (CF_3)_2P(O)Cl$$
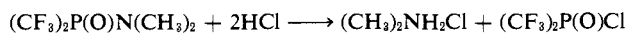
also becomes quantitative, providing a convenient and efficient new approach to fluorocarbon–phosphinyl chemistry.

In the phosphinic amide the electronegativity of the CF_3 groups would induce strong N_{2p}–P_{3d} dative π-bonding, so that nitrogen base action would be fairly weak. This expectation is confirmed by the easy dissociation of the BF_3 complex and by the difficulty of converting the amide wholly to the chloride by low-pressure HCl.

The experimental work here described was performed by means of a high-vacuum manifold, with U-traps in series for separations by fractional condensation. Halocarbon-greased stopcocks were used for oxidizing materials; otherwise mercury float valves were used to permit more accurately quantitative manipulation of volatile materials.

The Nitrogen Dioxide Oxidation. Six experiments employed roughly equimolar proportions of $(CF_3)_3P$ and NO_2 (determined by weight) in a reaction tube attached to the high-vacuum system and closed by a stopcock. In the first three experiments, the brown color faded out during 1 hr. at 25°; but when a special effort was made to eliminate all iodide impurities, such as CF_3I or $(CF_3)_2PI$, the process became one-third as fast. Hence it is possible that the oxidation requires at least a very faint trace of iodide impurities for catalysis.

From 2.1865 mmoles of highly purified $(CF_3)_3P$ with 2.23 mmoles of NO_2, the yield of $(CF_3)_3PO$ was 2.184 mmoles, or 99.8%. In other experiments the recovery averaged 95%. In three experiments, the recovery of NO was quantitative: 1.05, 0.53, and 7.30 mmoles of NO_2 yielded 1.05, 0.53, and 7.32 mmoles of NO, respectively. For such a result it was necessary to perform repeated fractional condensations (at $-120°$) to overcome the solubility of the NO in the $(CF_3)_3PO$. The NO was identified by its volatility and molecular weight (29.6 and 29.8 vs. 30.0 calcd.). The vapor-phase molecular weight of the phosphine oxide was determined as 255.7 or 253.9 (254.0 calcd.).

Physical Properties of the Phosphine Oxide. The melting point of a well-purified sample of $(CF_3)_3PO$ was determined by the Stock magnetic plunger method, using a carbon dioxide vapor tension thermometer. The average of four determinations was $-88.8°$ (range, 0.66°). Typical equilibrium vapor pressures are shown with an equation in Table I. The calculated boiling point is 32.34° vs. the directly observed value 32.0°. The Trouton constant is 22.1 e.u.

The Aminolysis Reaction. The reaction of $(CF_3)_3PO$ with $(CH_3)_2NH$ (slight excess) was signaled by white fumes which appeared well below room temperature. The components were separated by fractional condensation under high vacuum, at -78, -120, -140, and $-196°$, cleanly yielding in order $(CF_3)_2P(O)N(CH_3)_2$, excess amine, and HCF_3. No $(CF_3)_3PO$ could be found. In one experiment, 0.75 mmole of $(CF_3)_3PO$

consumed 0.75 mmole (from 0.84) of $(CH_3)_2NH$; recovered were 0.70 mmole of HCF_3 and 0.74 mmole (ca. 99%) of $(CF_3)_2P(O)N(CH_3)_2$. In another experiment, a 1.77-mmole process yielded 1.74 mmoles (98%) of HCF_3 and 1.68 mmoles of the amide. The identity of the HCF_3 was checked by its infrared spectrum, and good purity was indicated by its molecular weight (69.6 vs. 70.0 calcd.). Thus the quantitative stoichiometry demonstrated the composition corresponding to the formula $(CF_3)_2P(O)N(CH_3)_2$. The vapor-phase molecular weight (229.4 and 230.3 vs. 229.0 calcd.) then confirmed this as the molecular formula. The purity of the substance was indicated by its physical properties and the behavior of its BF_3 adduct.

Table I. Vapor Tensions of $(CF_3)_3PO$
($\text{Log } P = 4.5070 + 1.75 \log T - 0.003154T - 1531/T$)

Temp., °C.	−78.0	−49.6	−39.5	−32.1	−23.1	0.00	32.5
P_{obsd}, mm.	1.15	11.66	22.9	36.3	62.2	201.2	757.0
P_{calcd}, mm.	1.13	11.62	22.8	36.6	61.8	201.5	763.6

The vigorous aminolysis of $(CF_3)_3PO$ contrasts with the inert behavior of $(CF_3)_3P$ toward $(CH_3)_2NH$. With $(CH_3)_3N$, this phosphine shows no more than a deviation toward vapor tension values lower than for an ideal mixture; no specific adduct can be demonstrated. Most probably the aminolysis of $(CF_3)_3PO$ is an S_N2 process, such as $(CF_3)_3P$ cannot match.

Physical Properties of the Phosphinic Amide. The compound $(CF_3)_2P(O)N(CH_3)_2$ melted sharply at $-21.07°$. Its equilibrium vapor pressures are represented in Table II, with the boiling point calculated as 154.6° and the Trouton constant as 21.06 e.u. The equation is based upon 21 actual points.

Table II. Vapor Tensions of $(CF_3)_2P(O)N(CH_3)_2$
$\text{Log } P = 7.4772 + 1.75 \log T - 0.006323T - 2779/T$

Temp., °C.	23.0	32.4	42.2	49.9	59.9	67.6	72.8
P_{obsd}, mm.	3.55	6.30	10.9	16.9	28.0	40.1	50.2
P_{calcd}, mm.	3.51	6.29	11.1	16.8	28.1	39.9	50.3

The Boron Fluoride Adduct. The phosphinic amide with excess BF_3 formed a solid adduct which did not melt at 25° until after the excess BF_3 had been removed by distillation from a trap at $-130°$. For example, 0.466 mmole of the amide with 0.786 mmole of BF_3 yielded back 0.31 mmole of BF_3, leaving $1.02BF_3$ per amide. The BF_3 was rechecked by its molecular weight and infrared spectrum. The remaining 1:1 adduct weighed 139.3 mg. (138.4 calcd.). Two further experiments of the same kind gave essentially the same results.

With no excess BF_3, the adduct showed a melting range beginning at about 20°. This effect could be understood in terms of the dissociation pressures, representative examples of which are shown in Table III. These results determined the equation $\log P = 11.1070 - 2995/T$. A scan of the vapor by the Infra-

cord spectrophotometer showed only the bands corresponding to the components, BF_3 and the amide; hence, it was considered that the pressures represented essentially complete dissociation of the adduct. Hence for pressures in atmospheres, $\log K = 15.8503 - 5990/T$, meaning that $\Delta F = 27.42 - 0.07257T$ kcal. for the dissociation of 1 mole of the adduct.

Table III. Dissociation Pressures of the Amide–BF_3 Adduct

Temp., °C.	2.1	5.2	7.5	10.0	12.1	15.0	18.0
P_{obsd}, mm.	1.70	2.25	2.77	3.35	4.02	5.15	6.62
P_{calcd}, mm.	1.68	2.25	2.73	3.38	4.04	5.18	6.60

By these results, the partial pressure of the amide would equal its condensation pressure at a point just below 20°, above which the liquid would form and more BF_3 would be liberated than corresponds to the dissociation–pressure equation. Thus there could be no true melting point, but only a point at which a range begins, and obviously excess BF_3 would stabilize the solid.

Conversion of the Phosphinic Amide to Chloride. Three exploratory experiments indicated that $(CF_3)_2P(O)N(CH_3)_2$ with little more than 2HCl at normal pressures would react only very slowly at 25° (55% in 48 hr.) and scarcely better at 52° (53% in 46 hr.) or at 100° (48% in 20 hr.). It seemed that the rate in the vapor phase was minimal; also reversibility was suspected. Hence, for efficient action, 1.282 mmoles of the amide and 5.666 mmoles of HCl were allowed to react in a 10-ml. sealed tube (14 atm. initial HCl pressure) during 14 hr. at 24°. The resulting mixture was resolved by high-vacuum fractional condensation (at -70, -120, and $-196°$), showing the stoichiometry (mmoles, from gas volumes except where "wt." is specified) accompanying the following equation.

$$
\begin{array}{cccc}
(CF_3)_2P(O)N(CH_3)_2 & + & 2HCl & \rightarrow & (CH_3)_2NH_2Cl & + & (CF_3)_2P(O)Cl \\
1.282 \text{ (by wt.)} & & 5.666 & & 1.29 \text{ (wt.)} & & 1.260 \\
-0.020 & & -3.101 & & & & (98.3\%) \\
\hline
1.262 & & 2.565 & & & &
\end{array}
$$

The recovered HCl showed no HCF_3 infrared bands. The unused amide (-0.20) was identified by its volatility at 24° (3.5 mm.) and molecular weight (229, as calculated). The product $(CF_3)_2P(O)Cl$ also was confirmed by its volatility (88.6 mm. at 0°, in accord with the known equation)[3] and molecular weight (221.4 vs. 220.5 calcd.).

In sum, then, it now is possible to convert $(CF_3)_3P$ by way of three quantitative steps to $(CF_3)_2P(O)Cl$, from which the full chemistry of the phosphinyl group $(CF_3)_2PO$ can be developed.

Exploratory attempts to convert the phosphinyl amide to the chloride by means of PCl_5 or $SbCl_5$ were not promising; the recovery of the desired product was poor or even nil, apparently on account of adduct formation. Especially the $SbCl_5$ adduct deserves fuller study.

Infrared Spectra. The frequencies of the band maxima for the recognizable fundamental vibrational

(3) J. E. Griffiths and A. B. Burg, *J. Am. Chem. Soc.*, **84**, 3442 (1962).

modes of $(CF_3)_3PO$, $(CF_3)_2P(O)N(CH_3)_2$, and $(CF_3)_2P(O)Cl$ are listed in Table IV with relative intensities (in parentheses) defined by the arbitrary equation $k = (100/PL) \log I_0/I$ for pressure P (reduced to 25°) and path L, both in cm. PL values ranged from 0.2 to 104, for recording the weakest and strongest peaks. The windows were NaCl, KBr, or high-density annealed polyethylene, as appropriate.

Table IV. Fundamental Infrared Peaks (cm.$^{-1}$)[a]

Expected mode	$(CF_3)_3PO$	$(CF_3)_2P(O)N(CH_3)_2$	$(CF_3)_2P(O)Cl$
C–H stretching	...	2960 (3.0) 2927 (1.7) 2884 (1.4) 2848 (0.6)	...
CH_3, δ-a	...	1495 (1.2) 1468 (1.8)	...
CH_3, δ-e	...	(covered ?)	...
P=O stretching	1349 R (0.8) 1327 Q (12) 1307 P (1.2)	1330 (13)	1332 R } 1327 P } (16)
C–F stretching	1220 sh (145) 1210 (300) 1184 (61)	1204 (58) 1167 (33) 1127 (7)	1199 (95) 1157 sh (4)
C–N stretching	...	1079 (1.1)	...
CH_3 rocking	...	995 (14)	...
CF_3, δ-e	770 (0.30) 753 R (0.20) 749 Q (0.37) 743 P (0.18)	758.5 (1.7)	760 sh (0.42) 755 (0.54)
P–N stretching	...	712.5 (7)	...
P–Cl stretching	...	...	616.5 (17)
CF_3, δ-a	583 (6.5)	571 (9)	563.5 (8) 541 } 536 } (2.6)
P=O bending	500.5 (3.1)	502 (4.7)	504 (6)
P–CF_3 stretching	409.5 (1)	412 (0.6)	418 (2.2)
CF_3 rocking (with P–Cl bend)	280 (0.26) 264 (0.12) 258.5 (0.14)	325 (1.0)	342.5 (0.34) 278 (0.30) 274 (0.35) 249.5 (0.59)

[a] Abbreviations: sh, shoulder; δ, deformation; a, asymmetric; e, symmetric.

Weak bands not securely attributable to impurities, and so presumed to represent mostly overtones and combinations, are listed with k values in parentheses, as follows: for $(CF_3)_3PO$, 2395 (0.37), 2366 (0.45), 2314 (0.64), 1953 (0.15), 1930 (0.08), 1452 (0.04), 1396 (0.16), 1375 (0.33), 1287 (1.0), 1105 (0.28), 1084 (0.20), 1064 (0.16), 1032 (0.20), 1012 (0.17), 950 (0.06), 902 (0.07), 795 (0.06), 720 (0.17), and 619 (0.25), all in cm.$^{-1}$. For the amide, such weak bands were not seen, for the highest PL number for this less volatile substance was only 10. For $(CF_3)_2P(O)Cl$ the CF_3 stretching overtones and combinations formed a rough pattern of peaks and shoulders in the range 2300–2420 cm.$^{-1}$, with the highest k value = 0.31, occurring at 2350 cm.$^{-1}$. Distinct peaks appeared also at 1038 (0.09), 942 (0.03), and 908 (0.08) cm.$^{-1}$.

Although infrared spectra have been reported for two

of these compounds in the prior literature,[2,3] the present results are regarded as more accurate as well as more extensive. By the application of calibrations based

upon very well-known peaks, the probable error in the present work should not exceed 1 cm.$^{-1}$ for regions below 2000 cm.$^{-1}$.

Nucleophilic Constants and Substrate Discrimination Factors for Substitution Reactions of Platinum(II) Complexes

Umberto Belluco, Lucio Cattalini, Fred Basolo, Ralph G. Pearson, and Aldo Turco

Contribution from the Chemical Laboratory of Northwestern University, Evanston, Illinois, and the Istituto Chimica Generale, Universita di Padova, Padova, Italy. Received July 15, 1964

The kinetics for the substitution reactions of six different platinum complexes of the type trans-[PtL$_2$Cl$_2$] with eighteen different nucleophilic reagents are reported. A set of nucleophilic reactivity constants, n$_{Pt}$, are defined for these reagents by selecting trans-[Pt(py)$_2$Cl$_2$] as a standard. Other platinum complexes then obey the equation log k$_Y$ = sn$_{Pt}$ + log k$_S$, where k$_Y$ is a second-order rate constant for the nucleophile Y, s is a nucleophilic discrimination factor, and k$_S$ is an "intrinsic" reactivity measure which is equal to the first-order rate constant for the reaction in which the solvent is the nucleophile. Complexes with a low intrinsic reactivity have a large value of s, and complexes which are highly reactive show little discrimination. Strong π-bonding ligands, in the cis position, produce low values of k$_S$ but large values of s.

Introduction

The chemical literature contains a large amount of data on rates of bimolecular, nucleophilic substitution reactions.

$$Y + M-X \longrightarrow M-Y + X \qquad (1)$$
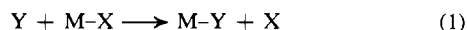
Here M is an electrophilic atom, which will be a metal in the cases of interest in this paper, Y and X are nucleophilic atoms or groups also called ligands, and M has other inert groups or ligands attached to it. The mechanism is the familiar S_N2 process in which a transition state, or possibly a reactive intermediate, of increased coordination number is formed with both Y and X bound to M. The substrate atoms (M), for which the most data are available,[1] include hydrogen, boron, carbon, nitrogen, oxygen, phosphorus, sulfur, platinum(II), and, more recently, palladium(II)[2] and gold(III).[3]

A number of attempts have been made to correlate the rates of eq. 1 with other kinetic and thermodynamic data as Y is varied. These are all based on the principle of linear free-energy relationships.[4] Some of these include the Brønsted relationship,[5] the Swain and Scott equation,[6] and the Edwards equations.[7] The latter are particularly interesting in that the oxidation potential of the nucleophile is taken as one of the parameters.

Recent discussions have emphasized the fact that no one scale of nucleophilic reactivity exists but that the substrate M–X determines the order of effectiveness of various Y groups.[1,8] In particular a simple, useful rule may be formulated. If we define a "hard" acid or base as one of low polarizability and a "soft" acid or base as one of high polarizability, then hard acids combine best with hard bases and soft acids combine best with soft bases.[8] The nucleophilic–electrophilic interaction in the transition state of reaction 1 is, of course, a generalized acid–base reaction. Thus, polarizable metal atoms such as platinum(II) will react rapidly with easily polarizable reagents (which are also those of more positive oxidation potential).

While there is ample evidence to substantiate the above statement,[8,9] there is relatively little evidence as to how changes in the nature of the leaving group X and the inert ligands changes the selectivity of platinum complexes toward a series of nucleophilic reagents. A previous conclusion[9a] that increased negative charge on the complex increases the relative reactivity toward polarizable reagents must be viewed with some caution. The conclusion was based largely on a comparison of rates of reaction with chloride ion and nitrite ion. We

(1) For a review and references, see J. O. Edwards and R. G. Pearson, *J. Am. Chem. Soc.*, **84**, 16 (1962).

(2) (a) R. G. Pearson and D. A. Johnson, *ibid.*, **86**, 3983 (1964); (b) W. H. Baddley, Doctoral Thesis, Northwestern University, Evanston, Ill., 1964.

(3) W. H. Baddley and F. Basolo, *Inorg. Chem.*, **3**, 1087 (1964).

(4) For a general discussion and for details of the various equations proposed, see J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1963, Chapter 9.

(5) J. N. Brønsted, *J. Am. Chem. Soc.*, **51**, 428 (1929).

(6) C. G. Swain and C. B. Scott, *ibid.*, **75**, 141 (1953).

(7) J. O. Edwards, *ibid.*, **76**, 1540 (1954); **78**, 1819 (1956); see also D. H. McDaniel and A. Yingst, *ibid.*, **86**, 1334 (1964).

(8) R. G. Pearson, *ibid.*, **85**, 3533 (1963).

(9) (a) F. Basolo and R. G. Pearson, *Progr. Inorg. Chem.*, **4**, 388 (1962); (b) H. B. Gray, *J. Am. Chem. Soc.*, **84**, 1548 (1962); (c) H. B. Gray and R. J. Olcott, *Inorg. Chem.*, **1**, 481 (1962).