In this proposed mechanism the $UO_2L^{2+}{}_{incl}$ decomplexation must proceed via the $UO_2L^{2+}{}_{excl}$ intermediate. The first preliminary remark above shows that k_d must be less than 0.022 s^{-1}. As this mechanism cannot explain the kinetic results, a mechanism is given (Figure 2) and discussed as follows.

In the first step (step I), which appears to be instantaneous when the stopped-flow technique is used, a direct interaction of the Na^+ ion with the $UO_2L^{2+}{}_{incl}$ complex gives rise to the $(UO_2L_{excl},Na)^{3+}$ intermediate species. This intermediate is probably an outer-sphere complex where the coordinating center $UO_2{}^{2+}$ is partially enclosed in the ligand cavity and where the Na^+ ion is incompletely desolvated. The $(UO_2L_{excl},Na)^{3+}$ complex is instantaneously in equilibrium (step II) with a second outer-sphere complex $(Na,UO_2L_{incl},Na)^{4+}$. In the $UO_2{}^{2+}$ ion, the effective electrical charge on the U atom is considerably higher than the total charge (+2) of the entity and the two oxygen atoms carry a net negative charge.[20] Then, two solvated Na^+ ions may enter into the second solvation shell of the $UO_2L^{2+}{}_{incl}$ complex and interact with the two oxygens of the uranyl ion. These fast steps I and II are followed by the total rotation of the uranyl group on the outside of the ligand cavity and by the uranyl–18-crown-6 bond rupture in the $(UO_2L_{excl},Na)^{3+}$ complex (step III). This last step is rate-determining and leads to the final product when the Na^+ ion has been completely and instantaneously buried in the host cavity. The $(Na,UO_2L_{incl},Na)^{4+}$ complex, in which the loss of the uranyl ion is hindered by the two Na^+ ions, would not give a rearrangement reaction leading to the NaL^+ complex. The mathematical treatment of this mechanism leads to the following equations, which agree with the experimental data:

$$-\frac{d[UO_2L]_T}{dt} = k_{obsd}[UO_2L]_T = k[(UO_2L_{excl},Na)^{3+}]$$

$$[UO_2L]_T = [(UO_2L_{excl},Na)^{3+}] + [(Na,UO_2L_{incl},Na)^{4+}]$$

$$k_{obsd} = \frac{k}{1 + K[Na^+]}$$

$$k = 0.41 \pm 0.02\ s^{-1};\ K = 890 \pm 30\ dm^3\ mol^{-1}$$

Only the third step is experimentally observed.

Some experiments done with Na^+ concentrations of 10^{-4}–10^{-3} M do not allow us to observe steps I and II, but the existence of these preliminary fast steps is supported by the measurement and the calculation of the absorbances corresponding to time zero for each kinetic experiment. The measured values are obtained by extrapolation of the experimental kinetic curves and the calculated ones by addition of the absorbances of each reactant after mixing and fast complexation of the excess free ligand. Small differences between these two values were observed, indicating fast preliminary steps.

Registry No. UO_2L^{2+}, 56508-54-4; Na^+, 17341-25-2.

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Carbonyl Difluoride: A Fluorinating Reagent for Inorganic Oxides

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Carbonyl difluoride (COF_2) has been demonstrated to be a highly versatile reagent for introducing fluorine into a variety of different molecules either by oxidative addition of fluorine to the central atom or by the displacement of hydrogen by fluorine from P–H, N–H, or C–H bonds.[1] We now report the results obtained when COF_2 is reacted with main-group and transition-metal oxides to provide a new simple route to useful fluorinated compounds.

Table I. Experimental Details of Fluorination of Inorganic Oxides with COF_2

group	reactant (2–3 mmol)	temp, °C	time, h	products: CO_2 +	yield,[a] %
5	V_2O_5	210	34	VOF_3	~100
	Nb_2O_5	200	36	NbF_5	~100
	Ta_2O_5	210	46	TaF_5	~100
6	CrO_3[b]	185	12	CrO_2F_2	~100
	MoO_3	190	31	$MoOF_4$	~100
	WO_3	180	48	WOF_4	~100
7	MnO_2	170	60	NR[c]	
8	OsO_4	90 or 150	22 (AHF)[f]	NR	
9	Co_2O_3	200	168	NR	
10	NiO	180	168	NR	
12	HgO (red)	160	36	NR	
	HgO (yellow)	200	36	NR	
13	B_2O_3	150	36	BF_3	~92
14	SiO_2	160	36	SiF_4	~100
	GeO_2	100	24	GeF_4	~84
	SnO_2[d]	220	70	SnF_4	~100
	SnO_2	210	80	SnF_4	~50
	PbO_2	200	24	NR	
15	P_4O_{10}	180	24	PF_5, OPF_3	~65
16	SO_2[d]	200	86	NR	
	SeO_2	200	50	$SeOF_2$	~100
	TeO_2	160	56	TeF_4	~100
17	I_2O_5	160	36	IF_5	~60
actinides	UO_3[e]	180	45	UO_2F_2	~100
	UO_3[d]	210	27	UO_2F_2	~100

[a] Based on CO_2 formed. [b] Reference 4. [c] No reaction. [d] In presence of small amount of CsF. [e] Reference 3. [f] Anhydrous hydrogen fluoride.

The conversion of inorganic oxides to fluorides can be accomplished in a large number of ways by using vigorous fluorinating reagents such as elemental fluorine or bromine trifluoride or with milder reagents such as anhydrous hydrogen fluoride or sulfur tetrafluoride. However, these fluorination methods often suffer from certain drawbacks, such as forming byproducts that are difficult to separate from the inorganic fluoride product or that are difficult to destroy. However, COF_2 is easily synthesized[2] and it reacts readily under mild conditions to form volatile CO_2 as the only byproduct. Carbon dioxide is easily removed from the reaction vessel and absorbed in alkali. Following the formation of the CO_2 via infrared spectral examination provides a good method for monitoring the progress of the reaction.

Experimental Section

General Procedure. A known amount (~2–3 mmol) of the anhydrous, powdered metal oxide or non-metal oxide was loaded into a 75-mL stainless steel or Monel Hoke cylinder fitted with a stainless steel or Monel Whitey valve. A slight excess over the stoichiometric amount of COF_2 required was condensed into the cylinder at −196 °C by using standard vacuum-line techniques (except SnO_2:COF_2 = 1:4 and Nb_2O_5:COF_2 = 1:8). The neat reaction mixture was then heated in an oven, with occasional shaking. After the reaction had finished, the presence of COF_2 and CO_2 was checked by examining their infrared spectra. All of the fluoride products were confirmed by comparison of infrared and ^{19}F NMR spectral data with literature values. *Caution*! Carbonyl difluoride is a highly toxic compound and should be handled accordingly.

Results and Discussion

Representative inorganic oxides were selected to cover most of the periodic table from group 5 to group 17. Oxides such as UO_3 were of particular interest in our static system since the fluorination of the former in a CO_2 flow system at 750 °C resulted in 97.6% conversion to UF_6.[3] We obtained essentially quantitative

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conversion of UO_3 to UO_2F_2 after 45 h at 180 °C. The presence of CsF does not give rise to further fluorination. The conditions and yields of our fluorinations are included in Table I.

With the exception of V_2O_5 that formed only VOF_3, group 5 oxides (M_2O_5) formed pentafluorides in essentially quantitative yield at $\sim$200 °C. In group 6, MoO_3 and WO_3 easily gave $MoOF_4$ and WOF_4 at $\sim$180-190 °C. Earlier, CrO_3 was shown to be converted quantitatively to CrO_2F_2.[4] Further fluorination of CrO_2F_2 with COF_2 either at higher pressure and higher temperature or by using anhydrous hydrogen fluoride as solvent was not possible. CrO_2F_2 was invariably recovered in quantitative yield. Commercial samples of WO_3 did not react with COF_2.

Oxides of groups 5, 6, and 16 show increasing reactivity with COF_2 on moving down the groups. However, in the case of group 14 dioxides, fluorination to MF_4 occurred with decreasing ease moving from SiO_2 to GeO_2, and finally, fluorination of SnO_2 occurred only at 220 °C in the presence of catalytic amounts of CsF. Lead(IV) oxide did not react. Carbonyl fluoride with P_4O_{10} gave a mixture of POF_3 and PF_5 (65% yield). In group 16, SO_2 did not react with COF_2 at 200 °C even in the presence of CsF and with longer reaction time (86 h). The reactions of COF_2 with either SeO_2 or TeO_2 proceed smoothly to form $SeOF_2$ or TeF_4 under conditions similar to those when SF_4 is used as a fluorinating reagent.

Fluorination of both I_2O_5 and B_2O_3 occurred very cleanly and at relatively low temperature. Trap-to-trap distillation gave pure IF_5 in 60% yield.

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Registry No. COF_2, 353-50-4; V_2O_5, 1314-62-1; Nb_2O_5, 1313-96-8; Ta_2O_5, 1314-61-0; PF_5, 7647-19-0; MoO_3, 1313-27-5; WO_3, 1314-35-8; MnO_2, 1313-13-9; OsO_4, 20816-12-0; Co_2O_3, 1308-04-9; NiO, 1313-99-1; HgO, 21908-53-2; B_2O_3, 1303-86-2; SiO_2, 7631-86-9; GeO_2, 1310-53-8; SnO_2, 18282-10-5; PbO_2, 1309-60-0; P_4O_{10}, 16752-60-6; SO_2, 7446-09-5; SeO_2, 7446-08-4; TeO_2, 7446-07-3; I_2O_5, 12029-98-0; UO_3, 1344-58-7; VOF_3, 13709-31-4; NbF_5, 7783-68-8; TaF_5, 7783-71-3; OPF_3, 13478-20-1; $MoOF_4$, 14459-59-7; WOF_4, 13520-79-1; BF_3, 7637-07-2; SiF_4, 7783-61-1; GeF_4, 7783-58-6; SnF_4, 7783-62-2; $SeOF_2$, 7783-43-9; TeF_4, 15192-26-4; IF_5, 7783-66-6; UO_2F_2, 13536-84-0.

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Synthesis of Tetramesitylporphyrin

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Metalloporphyrins have been largely used as oxygenation (i.e. hydroxylation and epoxidation) catalysts during the last 8 years.[1,2] They have been associated to various oxygen sources: PhIO, NaOCl, H_2O_2, ROOH, $KHSO_5$, or O_2 and electrons.

Efficient catalytic reactions are observed when the manganese or iron porphyrin is not transformed into an inactive μ-oxo entities or bleached via an intra- or intermolecular oxidation. This deactivation of the catalyst is very often avoided by using bulky porphyrin ligands in order to create a cage (in most cases it is an open well) around the active metal-oxo species. Such an open well effect has been obtained by using 2,6-disubstituted phenyl groups attached to the meso positions of synthetic porphyrins. Two ligands of this type have been largely used: tetramesitylporphyrin ($TMPH_2$) and tetrakis(2,6-dichlorophenyl)porphyrin in these metalloporphyrin-mediated oxygenation reactions.[3-8] The cage created by the methyl groups of the tetramesitylporphyrin allows also the isolation and characterization of high-valent metal-oxo species in the case of iron[9-11] or manganese[12,13] complexes.

The only limitation for general use of these bulky porphyrins is the tedious preparation according to the old Rothemund synthesis (aldehyde, pyrrole, and pyridine in a sealed tube) and its variations.[14,15] After purification, the yield of $TMPH_2$ preparation is in the range of 3-5%.[4] The recent report of Lindsey et al. of a new route for the preparation of tetraphenylporphyrins (preequilibration of pyrrole and benzaldehyde to the porphyrinogen at room temperature followed by an oxidation by a quinone under mild conditions) prompted us to try this new methodology in the preparation of a bulky porphyrin like $TMPH_2$.[16] Since we found that the yield of $TMPH_2$ by Lindsey's method reached 20%, but is sensitive to some experimental conditions, we wish to report in the present note the details of this preparation of $TMPH_2$ after modifications.

Experimental Section

Materials. Pyrrole (purum, Fluka) and mesitaldehyde (98%, Aldrich) were distilled under reduced pressure before use. 2,2-Dimethoxypropane, tetrachloro-*p*-benzoquinone (*p*-chloranil), and boron trifluoride-methanol complex were purchased from Janssen Chimica and used without further purification. Dichloromethane was distilled from CaH_2 under nitrogen before use. Alumina (activity I, neutral) was purchased from Merck.

Results

Synthesis of $TMPH_2$. A 1-L two-necked, round-bottom flask fitted with a reflux condenser and an argon inlet tube was filled with 500 mL of freshly distilled dichloromethane under a slight stream of argon and was magnetically stirred. Pyrrole (350 μL, 5 mmol), 2,2-dimethoxypropane (700 μL, 5.5 mmol), mesitaldehyde (750 μL, 5.5 mmol), and $BF_3 \cdot CH_3OH$ (100-200 μL, 0.91-1.82 mmol) were added in this order by use of syringes. After addition of $BF_3 \cdot CH_3OH$ the reaction mixture changes immediately from colorless to red-brown. The solution was stirred for 45 min at room temperature under a slow stream of argon. Then the solution was heated at 40 °C, tetrachloro-*p*-benzoquinone (400 mg, 1.6 mmol) was added, and the reaction mixture was maintained at slight reflux for 1 h (without argon bubling). After evaporation of the solution to dryness, the residue was redissolved in a minimum of CH_2Cl_2 and purified by chromatography over two successive dry columns of neutral alumina. From the first column (3.5 × 15 cm) with CH_2Cl_2 as eluent, one collected the first pink and green bands, combined these fractions, and evaporated them to dryness. The second chromatography column (3.5 × 15 cm) with toluene as solvent, gave first of all a pink band,

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