TABLE I

RATE CONSTANTS IN 50% BY VOLUME ACETONE–WATER AT 25°

	Benzyl bromide	$Si(acac)_3{}^{+a}$
k_{OH^-}	$1.6 \pm 0.1 \times 10^{-3}$ M^{-1} sec.$^{-1}$	1.7×10^3 M^{-1} sec.$^{-1}$
$k_{O_2H^-}$	$5.4 \pm 0.1 \times 10^{-2}$ M^{-1} sec.$^{-1}$	8.0×10^4 M^{-1} sec.$^{-1}$

[a] From reference 3.

TABLE II

H_2O_2, M	R_1/R_2 obs.	R_1/R_2 calcd.
0.10 Ethylenechlorohydrin 0.10 M base		
0.088	5.6	5.5
0.096	4.0	4.0
2.0	..[a]	..
None	..[b]	..
0.0029 M $Co(NH_3)_5Cl^{2+}$, 0.0029 M base		
0.018	3.6	3.7
0.013	2.3	2.8
2.0	..[c]	..
None	..[d]	..

[a] 2.4% base consumed in 10 minutes. [b] 37.5% base consumed in 10 minutes. [c] 2.5% chloride released in 10 minutes. [d] 62.5% chloride released in 10 minutes; data in water at 25°.

rate for hydroxide ion has also been measured. The solvent used was 50% by volume acetone–water and the analysis was by titration of released bromide ion. Good second order kinetics at 25° were observed for both reactions. The rate constants are given in Table I and it is seen that the O_2H^- ion is 35 times as reactive as the OH^- ion. Also shown are the two second order rate constants[3] for the bimolecular displacement reactions of the two anions on tris-(acetylacetonato)-silicon(IV) complex, $Si(acac)_3{}^+$, where it is observed that the O_2H^- ion is 50 times more reactive.

Results of this kind are more remarkable when it is recalled that hydrogen peroxide is nearly 10^4 times as acidic as water. Thus the equilibrium constant for the reaction

$$OH^- + H_2O_2 \longrightarrow H_2O + HO_2^- \qquad (2)$$

is 150 in conventional units. The existence of equilibrium (2) and the results quoted in ref. 1 and Table I allow an easy distinction to be made between an SN2 mechanism for a substrate which depends strongly on basicity in the nucleophile, and an SN1CB (dissociation of conjugate base) mechanism. In the former case the addition of excess hydrogen peroxide to a reacting mixture of substrate and hydroxide ion will lead to an *increased* rate of reaction by a factor which may be as large as 10^4. In the latter case there will be a *reduction* in rate by a factor as large as 150 for one molar H_2O_2. This is because an SN1CB reaction has a rate directly proportional to the hydroxide ion concentration and reaction (2) greatly reduces this concentration. Equation (3) gives the ratio of rates of release of halide ion, or reduction of concentration of alkali, for runs with (R_2), and without (R_1), added H_2O_2.

$$R_1/R_2 = 1 + 150[H_2O_2] \qquad (3)$$

Table II shows experimental values of R_1/R_2 compared to values calculated from (3) for several kinetic runs of the base hydrolysis of ethylene chlorohydrin and the chloropentammine cobalt(III) ion. These hydrolyses are generally believed to involve an SN1CB mechanism.[4] Values of R_1 found were in agreement with literature values. It is seen that hydrogen peroxide always inhibits the rate of halide release as predicted. Large amounts of hydrogen peroxide virtually stop the reaction as equation (3) predicts. Rapid decomposition of the peroxide occurs in these alkaline solutions,[5] especially in the presence of cobalt ion, some of which is reduced to cobalt (II). Nevertheless, the release of halide ion is small as Table II shows. The results with the chloropentammine cobalt(III) are of special interest because of recent claims that the base hydrolysis of this and similar complexes goes by an SN2 mechanism.[6]

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[3] R. G. Pearson, D. N. Edgington and F. Basolo, *J. Am. Chem. Soc.*, **84**, 3233 (1962).

[4] A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," Second Edition, John Wiley and Sons, Inc., New York, N. Y., 1961, pp. 288–305; R. G. Pearson, H. H. Schmidtke and F. Basolo, *J. Am. Chem. Soc.*, **82**, 4434 (1960).

[5] The rate of decomposition of H_2O_2 in alkali is given by Rate = $k[H_2O_2][O_2H^-]$; F. R. Duke and T. W. Haas, *J. Phys. Chem.*, **65**, 304 (1961).

[6] C. K. Ingold, R. S. Nyholm and M. L. Tobe, *Nature*, **194**, 344 (1962).

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FLUORIDE COMPLEXES OF PENTAVALENT URANIUM[1]

Sir:

We wish to report a new and direct synthesis yielding fluoride complexes of U(V) in high purity. The technique involves direct combination of UF_5 with ammonium fluoride at 80–85° or with alkali fluorides in a sealed bomb at 350–400°. The identity of these compounds with those crystallized from concentrated aqueous HF establishes that these latter compounds contain U(V) in the non-oxygenated state.

Alkali fluoride complexes of uranium such as $UF_4.nMF$ and $UF_6.nMF$ are well characterized. (Note: Although undoubtedly complex fluorides, we write them as addition compounds solely for ease in showing the uranium oxidation state.) Few comparable compounds of pentavalent uranium are known.

The compound $UF_5.3NaF$ was made[2] by limited fluorination of $UF_4.3NaF$. In a significant investigation published in report form, Rampy[3] found that UF_6 was reduced by NH_3 below 33° to form white $UF_5.NH_4F$. However, Galkin, *et al.*,[4] report that mixtures of UF_5 and $UF_4.NH_4F$ result from NH_3 reduction at 25°. It seemed de-

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[1] This work was sponsored by the U. S. Atomic Energy Commission.

[2] W. Ruedorff and H. Leutner, *Ann. Chem.*, **632**, 1 (1960).

[3] G. A. Rampy, GAT-T-697, 11-2-59, Goodyear Atomic Corp., available from U. S. Dept. of Commerce, Office of Tech. Services, Washington 25, D. C.

[4] N. P. Galkin, B. N. Sudarikov and V. A. Zaitsev, *Atomnaya Energiya*, **8**, 530 (1960), Consultant's Bureau Translation, **8**, 444 (1961).

sirable to investigate $UF_5.nMF$ systems starting with *uranium initially in the pentavalent state*, in particular, as UF_5.

Since it was known that NH_4F reacts smoothly with UF_4 under anhydrous conditions at 80–130° to form a series of complex fluorides,[5] we investigated the analogous reaction with pentavalent uranium. Both α and β forms of UF_5 react with NH_4F in 1:1 mole ratio to form $UF_5.NH_4F$ at 80–85°. In a typical preparation, ~50 mmol. of freshly prepared α-UF_5 was ground with 50 mmol. of dried NH_4F in a helium atmosphere. The mixture then was placed in a tightly closed polyethylene or Teflon container and heated for 2 days yielding a moisture-sensitive, nearly white product. *Anal.* Calcd. for $UF_5.NH_4F$: U, 64.32; NH_4, 4.86; F, 30.8. Found: U, 64.29; NH_4, 4.9; F, 30.0.

The product of heating NH_4F with UF_5 (1:1) at 85° has a characteristic X-ray powder pattern different from those of the starting materials. It suffers only negligible weight loss on heating several hours in vacuum (1μ) at 150° showing that no free NH_4F is present. It retains the X-ray pattern characteristics of $UF_5.NH_4F$. However, on treatment with water, white $UF_5.NH_4F$ disproportionates instantly, giving a solution containing yellow uranyl(VI) ion and a green solid having the X-ray pattern of rhombohedral $UF_4.NH_4F$.

If 48% HF is used to dissolve $UF_5.NH_4F$, a solution of U(V) is obtained as reported by Rampy.[3] In addition we find that UF_5 can also be dissolved with 48% HF without appreciable disproportionation.

On addition of a saturated solution of RbF dropwise to such solutions of U(V), the new compound $UF_5.RbF$ is precipitated as sizable ice-blue crystals. The X-ray powder patterns of $UF_5.RbF$ made from HF solution and $UF_5.NH_4F$ made under anhydrous conditions show that the two compounds are isostructural.

A pale blue powder is obtained by grinding together anhydrous RbF with UF_5 in a 1:1 mole ratio and heating for 16 hr. in a nickel bomb at 400°. The product gives a powder pattern identical with that of $UF_5.RbF$ obtained from HF solution. Without stabilization by formation of a fluoride complex, UF_5 disproportionates into UF_6 and lower fluorides at this temperature.[6]

The absorption spectra of solid $UF_5.NH_4F$ and $UF_5.RbF$ was measured from 4,000 to 17,000 Å. on a Cary Model 14 spectrophotometer. The spectra of the fluoride complexes containing pentavalent uranium are clearly different from those of fluoride complexes containing tetravalent uranium, particularly in the near infrared region.

Addition of H_2O_2 or Na_2SO_3 to an HF solution containing $UF_5.NH_4F$ causes reduction of U(V) to UF_4 which is insoluble in this medium. Uranyl(VI) is not reduced under these conditions. By this technique it was shown that when UF_5 or $UF_5.NH_4F$ is dissolved in 48% HF, >95% of the uranium is present as soluble U(V).

The technique of treating UF_5 with anhydrous fluorides seems to be generally applicable for preparation of U(V) fluoride complexes. We are in the process of extending this work and characterizing the resulting compounds, in particular those containing ratios of ammonium or alkali fluoride to UF_5 greater than 1:1.

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THE EXCHANGE OF CHROMIUM(II) ION AND *cis*-DIAZIDOTETRAAQUOCHROMIUM(III) ION. A DOUBLE-BRIDGED TRANSITION STATE[1]

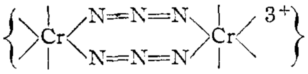
Sir:

Transition-states for many reactions of metal ion oxidizing agents and chromium(II) ion involve bridging between the metal atoms by a single ligand.[2] The possibility of a transition-state with two ligands bridging between the oxidizing agent and chromium(II) ion has been tested directly with negative results in two studies. In the oxidation of chromium(II) ion by either *cis*-diaquotetramminecobalt(III) ion or *cis*-diaquobisethylenediaminecobalt(III) ion, only one water molecule is transferred from the inner coördination sphere of cobalt to the inner coördination sphere of chromium.[3] Reaction of *cis*-difluorotetraaquochromium(III) ion and chromium(II) ion results in inappreciable exchange of chromium between the two species, but instead produces monazidochromium(III) ion, demonstrating the greater stability of a transition-state with one bridging fluoride ion relative to that with two bridging fluoride ions.[4]

In contrast to these results, we have observed direct exchange between chromium(II) ion and *cis*-diazidotetraaquochromium(III) ion:

$$Cr(N_3)_2^+ + {}^*Cr^{2+} = Cr^{2+} + {}^*Cr(N_3)_2^+$$

The only reasonable mechanism for this exchange reaction is "electron-transfer" *via* a transition state involving bridging between the chromium atoms by both azide ions:



If reaction of *cis*-diazidochromium(III) ion and chromium(II) ion had occurred *via* a transition-state with a single azide bridging group, net aquation would have resulted giving monazidochromium(III) ion and hydrazoic acid. The "irreversible" reaction of chromium(II) ion and hydrazoic acid to give nitrogen gas would preclude reentry of azide ion into the first coördination shell of chromium(III) by a pathway involving azide ion, chromium(II) ion and monazidochromium(III) species. Since chromium(II) was not consumed in the kinetic experiments and these

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[5] R. Benz, R. M. Douglass, F. H. Kruse and R. A. Penneman, "Preparation and Properties of Several Ammonium Uranium(IV) and Ammonium Plutonium(IV) Fluorides," being submitted to *Inorg. Chem.*

[6] J. J. Katz and G. T. Seaborg, "Chemistry of the Actinide Elements," John Wiley and Sons, Inc., New York, N. Y., 1957, p. 157.

[1] This work was supported in part by the United States Atomic Energy Commission under Contract AT(11-1)-1168.

[2] H. Taube, in "Advances in Inorganic Chemistry and Radiochemistry," H. J. Emeleus and A. G. Sharpe, editors, Vol. I, 1959, p. 1.

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[4] Y. T. Chia and E. L. King, *Disc. Faraday Soc.*, **29**, 109 (1960).