$\overset{+}{C}OHCH{=}CHC_6H_5$ is at 390 mμ in acetic acid with 20% by volume of sulfuric acid.[2] Further the λ_{max} values for the *p*-dimethylaminochalcones in sulfuric acid agree fairly well with that for the positive ion of chalcone, considering the bathochromic solvent effect of sulfuric acid on the principal bands of positive ions of unsaturated aldehydes and ketones. One must conclude that the bands observed at 483 and 490 mμ are not due to the second ions, but those observed at 425 and 396 mμ are.

In a solution of the singly charged positive ion of a tertiary amide, the tautomeric equilibrium $R_2\overset{+}{N}H\text{-}(R)C{=}O \rightleftarrows R_2\overset{+}{N}{=}C(R)OH$ is established. The interpolation of a phenyl or styryl group between the carbonyl and amino groups does not exclude this tautomerism, though it should greatly reduce the relative amount of the imidol tautomer, for its formation requires a change from a benzenoidal to a quinoidal structure. This quinoidal tautomer should absorb light in the visible. Hence the spectra obtained in acidified methanol show that the first ions of the *p*-dimethylaminochalcones are almost completely amido in methanol. The positive ion of *p*-nitrosodimethylaminobenzene is an example where the imidol or quinoidal tautomer is the more stable of the two.

Acetic anhydride would acetylate the quinoidal tautomer, thereby stabilizing a quinoidal structure. The formulas of the resulting acetates of the quinoidal forms of the first ions are $C_6H_5(CH_3CO_2)C{=}CH{-}CH{=}C_6H_4{=}\overset{+}{N}(CH_3)_2$ and $(CH_3)_2\overset{+}{N}{=}C_6H_4{=}C(O_2CCH_3)CH{=}CHC_6H_5$.

The formation of these acetates should be highly reversible. The positive charge of the ion is distributed by resonance over many atoms including the oxygen atom to which the acetyl group is attached. This makes these ions high energy acetates. The reformation of the benzenoidal tautomer also tends to reverse the acetylation. Hence acetic acid should react with these acetates to reform acetic anhydride to an anomalous extent. These expected reversals are shown in the published spectra. The bands of the benzenoidal ions (at 294 and 315 mμ) and those of the acetates of the quinoidal ions (at 483 and 490 mμ) appear on the same spectra.

The values of λ_{max} are reasonable for the structures suggested. The value of λ_{max} for the related compound $p\text{-}(CH_3)_2\overset{+}{N}{=}C_6H_4{=}C(C_6H_5)_2$ is 462 mμ in acetic acid. The replacement of a phenyl group by a styryl group would be highly bathochromic, while the replacement of the other group by an acetate group would be hypsochromic. Hence 490 mμ is a reasonable expectation for λ_{max} of $(CH_3)_2\overset{+}{N}{=}C_6H_4{=}C(O_2CCH_3)CH{=}CHC_6H_5$. The main cause of the color in both isomers is the conjugate system $\overset{+}{N}{=}C_6H_4{=}C{-}C{=}CC_6H_5$, so it is natural that the λ_{max} values of the two isomers are not very different.

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The Reaction of Fluorine with Titanium, Zirconium and the Oxides of Titanium(IV), Zirconium(IV) and Vanadium(V)[1]

BY H. M. HAENDLER, S. F. BARTRAM, R. S. BECKER, W. J. BERNARD AND S. W. BUKATA

RECEIVED NOVEMBER 10, 1953

Titanium reacts appreciably with fluorine above 150°, the vigor of the reaction depending on the size of the metal particles. Conversion is complete above 200°. Experimental quantities of titanium(IV) fluoride could be synthesized effectively by fluorination of massive titanium, preheated to 350° in the reactor.

Fluorine does not react appreciably with titanium(IV) oxide below 250°. Conversion is about 80% at 285° and complete at 350°. The titanium(IV) fluoride vaporizes and can be condensed.

Titanium(IV) fluoride is extremely hygroscopic; so much so that handling even in a dry-box becomes difficult. Apparently because of this the literature on X-ray powder patterns[2] is unreliable. The reported pattern is not that of titanium(IV) fluoride but is that of one or more reaction products of the fluoride with water. Work on this problem is in progress.

Fluorine reacts with zirconium metal above 190°. Fluoride coating of metal prevents complete conversion; the maximum obtained was about 90% at 420°. At higher temperatures product was lost.

Zirconium(IV) oxide does not react with fluorine at 100°, but converts to zirconium(IV) fluoride above 250°. Conversion is about 80% at 400°, 95% at 450° and complete at 525°. All lines in the X-ray powder patterns of the products could be attributed to oxide or fluoride. Comparison with prepared zirconium(IV) oxyfluoride showed its absence, which is in accord with its formation from oxide and fluoride only above 550°.[3]

Vanadium(V) oxide reacts with fluorine at 475° to form volatile vanadium oxytrifluoride, VOF_3, a reaction analogous to that reported for bromine trifluoride and the oxide.[4]

Experimental

The fluorinations were carried out in a manner similar to that previously reported.[5] An L-shaped nickel reactor was used with the titanium and vanadium oxides, the short side being cooled with Dry Ice. Titanium metal could be fluorinated successfully in glass, the volatilized fluoride being collected in an extension of the reactor tube. All product transfers were made in the dry-box.

Stock chemicals were used for the titanium and zirconium reactions. Vanadium(V) oxide was prepared by thermal decomposition of ammonium metavanadate.

Titanium was determined by ignition to the oxide with nitric and sulfuric acid or by precipitation with 8-quinolinol after removal of fluoride.[6]

Anal. Calcd. for TiF_4: Ti, 38.7. Found: $(Ti + F_2)$ Ti, 38.5, 38.7, 39.1; $(TiO_2 + F_2)$ Ti, 38.6, 39.2, 38.9.

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(1) Research supported by the Research Corporation and the Atomic Energy Commission.

(2) X-Ray Diffraction Data Cards, American Society for Testing Materials, Philadelphia, Pa.

(3) J. L. Williams, Report AECD-3335, Y-769, Oak Ridge National Laboratory, Feb. 15, 1951; "Nuclear Science Abstracts," Vol. 6, 1952, Abstract 2640, p. 337.

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Zirconium was determined by precipitation with mandelic acid after slow solution in sulfuric acid.[7]

Anal. Calcd. for ZrF_4: Zr, 54.6. Found: Zr, 53.7, 54.4, 55.0.

Vanadium was determined by precipitation with cupferron.[8]

Fluoride was determined by thorium nitrate titration after separation by distillation.[9] The original sample was fused with sodium hydroxide, treated with water, filtered, and the filtrate distilled.

Anal. Calcd. for VOF_3: V, 41.1; F, 46.0. Found: V, 42.2, 41.1, 40.7; F, 45.0.

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[8] G. E. F. Lundell, J. I. Hoffman and H. A. Bright, "Chemical Analysis of Iron and Steel," John Wiley and Sons, Inc., New York, N. Y., 1931, p. 78.

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The Reaction of Fluorine with Copper and Some of its Compounds. Some Properties of Copper(II) Fluoride[1]

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RECEIVED NOVEMBER 10, 1953

The action of fluorine on copper and several of its compounds is summarized in Table I. Copper(II) fluoride was formed in all cases.

TABLE I

FLUORINATION SUMMARY

Substance	Temp., °C.	Maximum conversion, %	Remarks
Cu	500	53	*a*
Cu_2O	150–325	. . .	*b*
	325–500	. . .	*c*
CuO	300–500	65	
$CuBr_2$	25–450	98	*d*
CuCl	100–550	~100	*e*
$CuCl_2$	200–550	~100	*f*
Cu_2S	25–550	5–100	*g*
CuS	25–550	~100	
$CuSO_4$	150–550	~100	*h*

[a] Resistant fluoride coating at lower temperatures, fusion and volatilization at higher. [b] X-Ray patterns showed Cu_2O, CuO and CuF_2 in mixture; see Fig. 1. [c] CuO in mixture began to react at about 300°. [d] Three refluorinations reduced bromide content to $< 0.15\%$. [e] Chloride present at 325°, absent at 550° after refluorination. [f] 94% conversion at 325°, chloride absent at 550° after refluorination. [g] 84% conversion at room temperature with undiluted fluorine; diluted fluorine gave 5, 20 and 63%, with X-ray patterns showing only Cu_2S and CuF_2. Refluorination at 550° gave sulfide-free product. [h] 4% conversion at 150°, 20% at 250°, 74% at 325°; sulfate-free after refluorination at 550°.

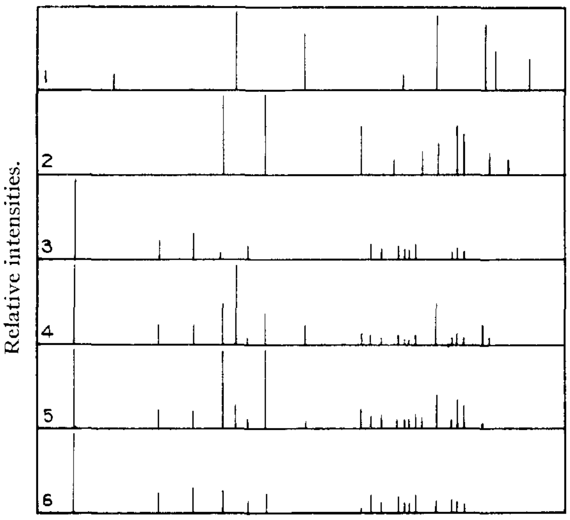

Fig. 1.—X-Ray pattern comparison for Cu_2O fluorination: 1, Cu_2O; 2, CuO; 3, CuF_2; 4, $Cu_2O + F_2$ at 200°; 5, $Cu_2O + F_2$ at 250°; 6, $Cu_2O + F_2$ at 325°.

The Density of Copper(II) Fluoride.—The density of copper(II) fluoride has been reported[2] as 4.23 g./cc., under somewhat ambiguous circumstances. The density of copper(II) fluoride, determined pycnometrically in benzene, was 4.85 ± 0.05 g./cc.

The Melting Point and Thermal Behavior of Copper(II) Fluoride.—The melting point of copper(II) fluoride has been reported[3] as 950 ± 5°, in an atmosphere of hydrogen fluoride. In a nitrogen or helium atmosphere the fluoride melted at 785 ± 10°. Considerable volatilization occurred below the melting point, and it was possible to vaporize samples completely at 850° in several hours. Powder patterns of various melts prepared by rapid heating in helium to 900–1000° showed only copper(II) fluoride lines. It was not possible to locate any lines due to metallic copper, although the position of these lines is not too favorable for distinction from the fluorides. This is in contrast to the reported formation of copper(I) fluoride[3] and subsequent disproportionation to copper and copper(II) fluoride.

The reactivity of the molten fluoride makes satisfactory study difficult, but an attempt was made to follow thermal changes by means of differential thermal analysis.[4] Runs with calcium fluoride and quartz powder as the supporting medium showed an endothermic peak at 770°, an exothermic peak at 780°, and a gradual, but very marked, endothermic change to 870–900°. This pattern suggests the possibility that copper(II) fluoride melts at 770°, decomposes at 780°, and that its decomposition product melts near 900°. At higher temperatures only calcium fluoride remained in the cell.

It was found that copper(II) fluoride reacted readily with nickel in helium at 900–950°. X-Ray powder patterns of the product showed only lines of copper and nickel(II) fluoride, in approximately equivalent amounts.

The Powder Pattern of Copper(II) Fluoride.—The crystal structure of copper(II) fluoride has been reported as the cubic fluorite type by Ebert and Woitinek,[2] although von Wartenberg[3] believed it to be of lower symmetry. X-Ray powder patterns have been made of the product of each reaction discussed above, and they are identical, re-

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[1] Research supported by the Research Corporation and the Atomic Energy Commission.

[2] F. Ebert and H. Woitinek, *Z. anorg. Chem.*, **210**, 269 (1933).

[3] H. von Wartenberg, *ibid.*, **241**, 381 (1939).

[4] We are indebted to Danford Q. Kelley, Geology Department, Massachusetts Institute of Technology, for these thermal analyses.