

BRIEF COMMUNICATION

Novel Solid State Reactions at Room Temperature

B. N. WANI AND U. R. K. RAO*

*Applied Chemistry Division, Bhabha Atomic Research Centre,
Bombay 400 085, India*

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Reaction between ammonium vanadate/sodium vanadate and bifluorides of the general formula MHF_2 , where $M = NH_4, Na,$ and K , in solid state at room temperature was investigated. It was found that the reaction readily takes place in all these cases by the transport of the HF_2^- ion along with its associated cation into the vanadate lattice, thus forming the corresponding crystalline oxyfluoro anionic compound. © 1991 Academic Press, Inc.

1. Introduction

The reactivity in solid state between two solids is diffusion controlled and complex. Most of the commonly studied reactions in solid state occur at elevated temperatures. These include synthesis by sintering, or alloy formation from metals, or simultaneous interdiffusion of two compounds. Even among reactions involving single crystal oxides, the reaction proceeds at different rates, depending upon the crystallographic faces of the solids which are in physical contact with each other. For instance, single crystals (1) of MgO and TiO_2 (Fe_2O_3 or Al_2O_3) have different rates of reaction when the (100) face of MgO is heated in contact with the (110) face of TiO_2 , compared to when the (110) face of MgO is in contact with the same (110) face of TiO_2 at $1550^\circ C$. There are other known cases where the re-

activity of one polymorph of a substance is totally different from the reactivity of another polymorph of the same substance toward another compound at nearly the same temperature. For instance, KHF_2 in the tetragonal phase does not react (2) at $180^\circ C$ with Nb_2O_5 even after heating for 3 hr, whereas the same KHF_2 , which undergoes a tetragonal to cubic phase transition at about $198^\circ C$, in its cubic form reacts readily with Nb_2O_5 at $210^\circ C$. Further, it is known that two metals (3), Fe and Zr , react to form an alloy at room temperature by ball milling, but the product is amorphous. During the past 10 years several examples (4-10) have been described in which two (or even three) solids, when mixed at room temperature and on application of minimum mechanical force, such as mixing with a pestle in an agate mortar, form a new product in a single phase. The most striking features of these reactions are:

(i) they readily take place between two

*To whom correspondence should be addressed.

crystalline solids at room temperature as though they involved ionic compounds in solution, and

(ii) the product is also crystalline.

It is difficult to rationalize the latter observation. Because the two reacting solids have totally different static structures at room temperature, merely mixing them results in a third solid with a structure entirely different from that of the either reactant. The formation of the product involves a complete change of symmetry and change of near neighbors, which necessarily results in translation, breaking of old bonds, and creation of new bonds, all taking place with almost no additional energy externally supplied except the thermal energy $K_{\beta}T$.

This paper describes a set of experiments in which this kind of reactivity is probed. The reactivity of three hydrogen fluorides MHF_2 ($M = K, NH_4,$ and Na) toward NH_4VO_3 and $NaVO_3$ is studied to investigate the mechanism of these reactions.

2. Experimental

The ammonium vanadate was of AR quality and the sodium vanadate was of GR quality. The metal hydrogen fluorides, i.e., KHF_2 and $NaHF_2$, are of LR grade, whereas NH_4HF_2 was supplied by Riedel-de Hang Chem. The powder XRD patterns of all the starting compounds matched those reported in the literature. Cylindrical samples 6 mm/12 mm in diameter and about 10 mm in height were made by cold pressing the powders at room temperature in a press at 4000 kg/cm^2 . The XRD powder patterns of the products were recorded using nickel-filtered $CuK\alpha$ radiation.

The following reaction configurations were investigated:

(a) A pressed rod of 6-mm diameter and about 10 mm in height of one component was dipped into a loosely packed powder of the other component and kept undisturbed (Fig. 1A).

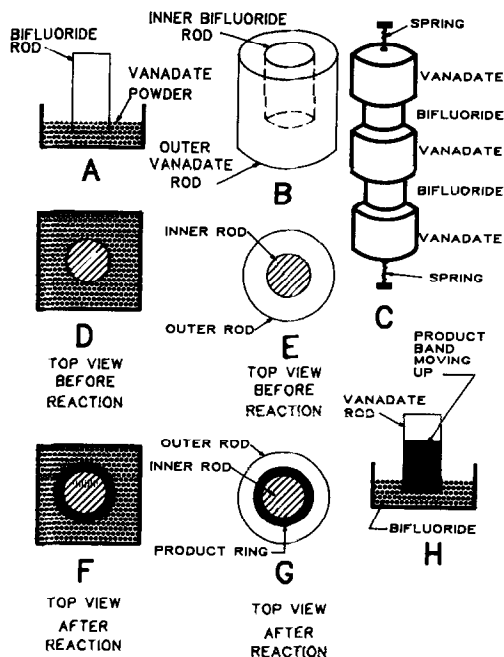


FIG. 1. Reaction configurations for different pairs of reactants.

(b) A 6-mm-diameter and 10-mm high pressed rod of one component was introduced into a 12-mm-diameter die, and the annular space was filled with powder of the other component on all sides, including above the rod but not below the rod. The rod was pressed again in such a way that it yielded a composite pellet containing one component embedded in the pellet of the other component. The bottom face contains the surfaces of both the guest and the host flush with each other, as shown in Fig. 1B.

(c) In the third configuration, pellets of both components (one component with a 6-mm diameter and the other with a 12-mm diameter) were stacked one above the other alternately and the end pellets were spring loaded (Fig. 1C).

The top views of 1A and 1B are shown in Figs. 1D and 1E. The combinations of components in different configurations are given in Table I.

TABLE I
CONFIGURATIONS OF COMPONENTS

Serial No.	Configuration in Fig. 1	6-mm rod	Loose powder (P)/outer rod (R)
1	A	NH ₄ HF ₂	NH ₄ VO ₃ (P)
2	A	NaHF ₂	NH ₄ VO ₃ (P)
3	A	KHF ₂	NH ₄ VO ₃ (P)
4	A	NH ₄ HF ₂	NaVO ₃ (P)
5	A	NaHF ₂	NaVO ₃ (P)
6	A	KHF ₂	NaVO ₃ (P)
7	H	NH ₄ VO ₃	NH ₄ HF ₂ (P)
8	B	NH ₄ HF ₂	NH ₄ VO ₃ (R)
9	C	NH ₄ HF ₂	NH ₄ VO ₃ (R)

3. Results and Discussion

If MHF₂ is in the shape of a rod (Fig. 1A, Serial Nos. 1–6) or if MHF₂ is in the shape of an inner pellet (Fig. 1B, Serial No. 8), the progress of the reaction is manifest by the almost immediate development outward of a colored ring and by its subsequent growth around the bifluoride in such a way that the colored ring of the product formed is concentric with the circular cross-section of the bifluoride rod as shown in Figs. 1F and 1G. On the other hand, if the bifluoride is in the form of a powder and NH₄VO₃ in the form of a rod (Fig. 1H, Serial No. 7), the cylindrical surface above the bifluoride level becomes colored and the circular band travels upward against gravity as shown in Fig. 1H. In the case of alternate rods (Fig. 1C, Serial No. 9), the bifluoride enters the vanadate from both ends. Thus, irrespective of whether bifluoride is in the form of a rod or a powder, the reaction proceeds rapidly from the bifluoride toward the other component, and the reaction does not proceed at a discernible rate in the other direction even after a week. Thus, the reaction is unidirectional, with mass transport in one direction only, even against gravity (Fig. 1H). If the rate of growth of the radius of the ring is taken as a measure of the rate of the reac-

tion, this leads to a value of approximately 1×10^{-6} cm/sec in the case of the NH₄HF₂/NH₄VO₃ pair of reactants. The colored product was carefully separated in the cases of the pairs in Serial Nos. 1, 2, and 3 and their powder XRD patterns were recorded. The product of 1 was identified as [NH₄]₃VO₂F₄. The colored products from 2 and 3 yielded distinct XRD patterns of their own, but different from that of 1. These two are being identified. Since in all cases the progress of the reaction is from the bifluoride toward the other component, it is doubtful that any HF vapors emanating from the bifluoride at room temperature are responsible for the reaction. If that were true, the colored product in 1, 2, and 3 should be identical, which is not the case. The bifluoride, along with the associated cation, is migrating and reacting with the other component.

All the bifluorides except ammonium bifluoride have a tetragonal structure (11) at room temperature, whereas the ammonium compound has an orthorhombic structure. In all cases the linear HF₂⁻ groups occupy a lattice site. The fact that the metal bifluoride is the labile compound and always moves into the other component probably results from both the thermal vibrations of the anionic group and the open structure of the other component.

Whether there is any heat of reaction between the two solids on mixing at room temperature is being investigated by mixing them at a temperature much below ambient and slowly warming the mixture, with simultaneous monitoring of temperature.

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