

ISOMERISM IN INORGANIC CHEMISTRY

BY

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In 1828 Wöhler discovered that urea may be formed by heating ammonium cyanate. This discovery marked the beginning of a new era in organic chemistry, for it proved that there is no fundamental difference between organic and inorganic compounds. It had another result, the significance of which was not realized at the time; it stimulated the study of isomerism and molecular structure. Earlier investigators had reported a few cases in which two substances of the same composition showed different properties, but these had received scant attention. Wöhler's discovery was so striking that every aspect of it was subjected to investigation and discussion; one such aspect was the fact that the ammonium cyanate and the urea contained the same elements in the same proportion, yet they are very different compounds. This naturally led to a study of the structure of the two molecules. It is interesting to note that this first pair of isomers is composed of one inorganic and one organic substance. Many hundreds of cases of isomerism are known now; most of these are among the carbon compounds, and many people have come to consider isomerism as being typical of organic chemistry.¹

There is little basis for this attitude. Indeed, among the inorganic substances we may find as many types of isomerism as among the organic compounds. Many naturally occurring substances are found in two or more forms. In some cases, as with calcite and aragonite, the forms seem to differ only in crystalline structure; in others, as with pyrite and marcasite, there is a decided difference in chemical properties. Pyrite dissolves completely in concentrated nitric acid, but marcasite leaves a residue of sulfur. Naturally occurring mercuric sulfide is red; that prepared by the reaction of a mercuric salt with hydrogen sulfide is black. This is not due to a difference of particle size, for the red sulfide retains its color even when very finely powdered. It may be changed into the black form only by sublimation. Natural and artificial antimony sulfide show a similar difference in color. The cause for

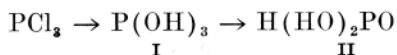
¹ See, for instance, Holleman, *Text-book of Organic Chemistry*, translated by Walker, Fifth English Edition, page 3, John Wiley and Sons, 1920.

these differences is not known. Many crystalline substances, such as quartz, show optical isomerism because of the arrangement of the atoms in the crystal lattice. This is shown also by some synthetic chemicals, such as sodium chlorate. The optical activity is lost when the material is in solution.

The structure of the complex cobalt ammines and similar compounds has received much study. These substances furnish examples of both structural and geometrical isomerism. However, we shall confine ourselves here to a discussion of the isomerism of the simpler molecules.

Some text-books give the structural formula for sulfurous acid as $(\text{HO})_2\text{SO}$, basing this upon the fact that sulfurous acid is formed by hydrolysis of SOCl_2 . Others write the formula as $\text{H}(\text{HO})\text{SO}_2$, which explains the fact that one of the hydrogen atoms is much more easily replaced than the other. Schwicker² upheld the second formula, basing his contention upon his claim to have prepared two isomeric potassium sodium sulfites, $\text{K}(\text{NaO})\text{SO}_2$ and $\text{Na}(\text{KO})\text{SO}_2$. Fraps and Remsen³, however, were unable to repeat this work. It is probable that sulfurous acid exists in two tautomeric forms, $(\text{HO})_2\text{SO} \rightleftharpoons \text{H}(\text{HO})\text{SO}_2$.

Similarly, phosphorous acid may have two structures, $(\text{HO})_3\text{P}$ and $\text{H}(\text{HO})_2\text{PO}$. Phosphorous acid prepared by hydrolysis of the chloride shows much greater reducing power when first formed than it does after standing for a time. This would indicate that some isomeric or tautomeric change takes place. Perhaps the reaction is



Compound I, in which the phosphorus atom has a valence of three would be expected to be a stronger reducing agent than compound II, in which the phosphorus has attained its maximum valence.

Similarly nitrous, arsenious, cyanic, hydrocyanic, and many other acids may each be given two structural formulae. Each of these will explain some properties of the substance, but neither of them will explain all. This is true also of hydrogen peroxide, to which the formulae $\text{H}-\text{O}-\text{O}-\text{H}$ and $\text{H}_2=\text{O}=\text{O}$ have been assigned. If we could isolate isomeric forms of the acids or of their salts, our knowledge of the structure of these molecules might be greatly increased. With this hope in view, we have begun a study of the isomerism of some simple inorganic molecules. This study has not proceeded far—the results here reported are only preliminary.

² Schwicker, Ber., 22: 1733 (1899).

³ Fraps and Remsen, Am. Chem. J., 22: 202 (1901).

Rathke⁴ has prepared sodium selenosulfate, Na_2SSeO_3 , by boiling selenium with sodium sulfite solution. The writer attempted to prepare the isomeric sodium thioselenate by boiling sulfur with sodium selenite solution. No reaction took place. Selenium does not assume the valence of six as easily as does sulfur. But when sodium selenite was heated to 120° with sulfur in a sealed tube, a reaction did take place. The material which was formed is soluble in water, and when acid is added to the solution, a precipitate of sulfur is formed. This is just the reaction we should expect from sodium thioselenate. The material which gave this reaction is present in only a small amount, and so far it has not been possible to obtain it in the pure state.

Another pair of isomers which we are studying consists of thallic oxychloride and thallous hypochlorite. We have prepared the oxychloride by shaking two equivalent weights of thallic hydroxide with one equivalent weight of the chloride in solution. The reaction is very slow, due to the extreme insolubility of thallic hydroxide. For the preparation of thallous hypochlorite ice cold solutions of thallous sulfate and barium hypochlorite were mixed. Barium sulfate was precipitated; after a few minutes the solution suddenly deposited a copious precipitate of thallic hydroxide. The thallous hypochlorite is evidently too unstable to exist long, even at low temperatures. The writer is now turning attention to the preparation of thallic oxychlorate, TlOClO_3 . The isomeric thallous perchlorate has been described in the literature.

One other pair of isomers is being considered for immediate study. These are uranyl sulfite, UO_2SO_3 , and uranous oxysulfate, UOSO_4 . The first of these has been prepared by Kohlschutter⁵; the second is a well known substance. It is proposed to study the relative stabilities of these two compounds, and to effect the rearrangement of one into the other. The corresponding selenium compounds will also be studied.

⁴ Rathke, *J. Prakt. Chem.*, 95: 1 (1865).

⁵ Kohlschutter, *Ann.* 311: 1 (1900).