

On the Mercury PhotoSensitized Reactions of Ethylene

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The Crystal Structure of Hexagonal Barium Titanate¹

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April 15, 1948

TWO modifications of barium titanate have been described by Blattner, Matthias, and Merz² from studies on single crystals. The well-known cubic form (tetragonal and ferroelectric below the Curie point at 120°C) has the perovskite structure. We have now studied single crystals of the hexagonal form by x-ray diffraction and derived its structure. The results show that the two structures differ only in the manner of close-packed stacking of BaO₃ layers of atoms.

A series of Buerger precession photographs gave the following data for the hexagonal crystals.

Crystal class: hexagonal, 6/mmm
Cell dimensions: $a_0 = 5.735\text{\AA}$, $c_0 = 14.05\text{\AA}$
Space groups: $C6_3/mmc = D_{6h}^4$
Cell content: 6 formulas BaTiO₃.

The photographs show many systematic absences of reflections characteristic of the structure so that the space group is not immediately evident. The structure was therefore investigated on the basis of lattice and cell dimensions, exclusive of details of symmetry. There is a very close relationship between these dimensions and those of the cubic form, with a cube edge $a_{\text{cub}} = 4.02\text{\AA}$. The hexagonal cell fits almost exactly into the cubic lattice; thus, $a_{\text{hex}} = \sqrt{2}a_{\text{cub}}$; $c_{\text{hex}} = 2\sqrt{3}a_{\text{cub}}$. This means that the hexagonal structure must consist of close-packed BaO₃ layers of atoms as found in the cubic form lying parallel to the (111) planes. The structure problem, therefore, is one of finding all the possible ways of stacking these close-packed layers to give a six-layer repeat unit.³

There are only five such structures with a repeat unit of six layers or less. Using the conventional symbols *A*, *B*, and *C* to locate close-packed layers with respect to one another, these structures are: (I) *AB*, (II) *ABC*, (III) *ABCACB*, (IV) *ABCBCB*, and (V) *ABCB*. The titanium atoms will be located in the oxygen octahedral holes

between the layers. The zero level *c* axis photograph shows that the reflections (*hk*·0) occur only when $h - k = 3n$. This can only be true if there is an equal number of layers *A*, *B*, and *C* within the cell. Thus, structures I, IV, and V are ruled out. Structure II is cubic close-packed and corresponds to the perovskite structure of the cubic barium titanate. Therefore, the only structure remaining for the hexagonal form is structure III. The parameters for this structure give good agreement between calculated and observed intensities.

The structures of the cubic and hexagonal forms are shown in Fig. 1. The cubic form contains TiO₆ octahedra linked to neighboring octahedra by corners throughout the structure. The hexagonal structure has the unusual feature of two TiO₆ octahedra sharing a face, forming a Ti₂O₇ group in the structure. The remaining third of the titanium atoms lies in single octahedra, linked by corners to these double groups. The two titanium atoms in the double group are strongly repelled by each other and are separated by about 2.96Å (distance between octahedral centers, 2.35Å). This Ti-Ti distance is almost identical with that found in rutile.

If these face-shared groups are allowed, there is no reason to suppose that there is not a large number of hexagonal polymorphs of barium titanate. Our crystals were prepared by Dr. B. Matthias from melts containing titanium dioxide, and barium, sodium, and potassium carbonates. Their x-ray powder patterns are identical with that given by Megaw⁴ for a "rhombohedral" form. A search is being made for other polymorphs. The detailed investigation of atomic parameters in the hexagonal and other polymorphs of barium titanate will be reported in a later paper.

¹ This work is sponsored jointly by the Office of Naval Research and the Army Signal Corps, on Contract NSori-78, T.O. 1.

² H. Blattner, B. Matthias, and W. Merz, *Helv. Phys. Acta* **20**, 225 (1947).

³ This same problem was solved recently by Wells for the structure of CsCuCl₃: A. F. Wells, *J. Chem. Soc.* 1662 (1947).

⁴ H. D. Megaw, *Proc. Phys. Soc.* **58**, 133 (1946).

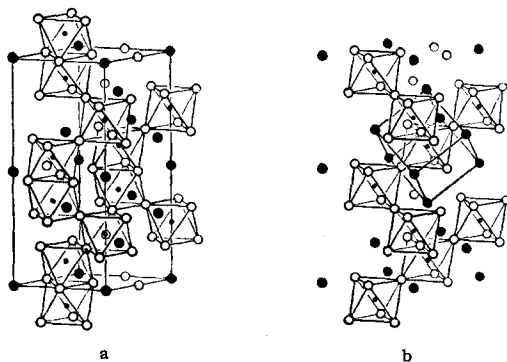


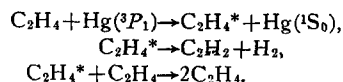
FIG. 1. Barium titanate crystal structure: (a) hexagonal form; (b) cubic form. Large black circles, barium; small black circles, titanium; large open circles, oxygen.

On the Mercury Photo-Sensitized Reactions of Ethylene*

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April 22, 1948

IN order to determine quantum yields for certain mercury photo-sensitized reactions which were being investigated, the authors attempted to measure the intensity of the mercury resonance line, $\lambda 2537$, entering their reaction cells by making use of the mercury photo-sensitized reactions of ethylene, for which LeRoy and Steacie¹ had reported the quantum yield of the initial stage as 0.37 at an initial ethylene pressure of 13 mm.

For the initial stage of this reaction, LeRoy and Steacie have proposed the following sequence:



On the basis of this mechanism, the rate of formation of acetylene, the rate of formation of hydrogen, and the rate of pressure increase are all equal, in agreement with LeRoy and Steacie's data.

In the authors' first set of five runs, the ratio of the rate of formation of hydrogen to the rate of pressure increase, averaged over the five runs, was found to be 1.29 ± 0.01 . The rate of pressure increase was determined from pressure measurements made with a McLead gauge. The hydrogen was determined by oxidation over oxide. Acetylene was not determined.

The second set of runs was carried out using a Hanovia Sc 2537 mercury resonance lamp. The incident intensity was varied over the range from 0.51×10^{-5} to 1.70×10^{-5} Einsteins per minute, as determined by uranyl oxalate actinometry,² by interposing oxidized bronze screens between the lamp and the cell. The pressure increase was measured to 0.01 mm by means of an automatic differential manometer of modified Pearson design.³ Hydrogen was determined simply as the gas non-condensable over liquid nitrogen, appropriate corrections being made. Acetylene was determined by the method of Ross and Trumbull.⁴ The average ratio, for six runs, of the rate of hydrogen formation to the rate of acetylene formation was 1.02, while the average ratio of the rate of hydrogen formation to the rate of pressure increase was 1.36. The quantum yield of hydrogen formation was 0.25.

All runs were carried out at an initial ethylene pressure of 13 mm. In all the experiments, the graph of pressure increase against time was linear, indicating that the data obtained referred only to the initial stage of the reaction.

The data given above indicate that in the authors' experiments, some pressure-reducing reaction, such as dimerization or polymerization, was present even in the initial stage of the reaction. The discrepancies between these data and those of LeRoy and Steacie may be due to differences in the characteristics of the lamps used, such as line breadth. Unpublished data from this laboratory suggest that for at least one substance the curve of initial rate of reaction against initial pressure of reactant was shifted and altered when one resonance lamp was substituted for another. Further work on the mercury photosensitized reactions of ethylene is under way in these laboratories in order to attempt to resolve the discrepancies reported.

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² G. S. Forbes and L. J. Heidt, *J. Am. Chem. Soc.* **56**, 2363 (1934).

³ D. J. LeRoy, *Ind. Eng. Chem.* **17**, 652 (1945).

⁴ W. H. Ross and H. L. Trumbull, *J. Am. Chem. Soc.* **41**, 1180 (1919).

Concentration of N¹⁵ in a Gaseous Exchange Column

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April 7, 1948

IN a previous communication¹ from this laboratory a concentration of C¹³ was reported using the reaction $C^{13}O + C^{12}O_2 \rightleftharpoons C^{12}O + C^{13}O_2$ in a gaseous exchange column.

TABLE I. Pressure = 0.5 atmos. Filament temp. = 500°C (approx.).

Time (days)	Over-all separation	Time (days)	Over-all separation
0.33	1.48 ± .05	6.0	3.00 ± .10
0.90	1.93 ± .06	7.0	2.79 ± .10
2.0	2.18 ± .06	7.5	3.00 ± .10
4.9	2.90 ± .10	8.0	3.10 ± .10
5.2	2.78 ± .10	12.0	3.14 ± .10
Equilibrium over-all separation = 3.00 ± .10			

Using the exchange reaction $N^{15}O + N^{14}O_2 \rightleftharpoons N^{14}O + N^{15}O_2$ in an apparatus similar to that already described, enrichment of N¹⁵ has been effected. The exchange was first suggested by Urey² as a possibility for the concentration of isotopic nitrogen, and experiments by Leifer showed the rate of the exchange to be very rapid even at low temperatures. Calculations of the equilibrium constant using the spectroscopic data given by Leifer and the method of Bigeleisen and Mayer³ gave values of 1.0146 at 200°C, 1.0075 at 400°C, and 1.0044 at 600°C.

The column constructed was 0.9 cm i.d. and 200 cm long. For the hot element a 0.64-mm Pt filament was used. NO₂ was circulated across the top from a 40-liter reservoir. The condition of reflux was satisfied by utilizing the reversible equilibrium $NO_2 \rightleftharpoons NO + \frac{1}{2}O_2$.⁵ With the wire temperature maintained at 500°C at a pressure of 0.5 atmos., an equimolar mixture of NO and NO₂ exists in the hot zone while recombination at the cold wall yields relatively pure NO₂. Since N¹⁵ preferentially concentrates in the NO₂ it is transported to the bottom by convective action in the cold stream. At the bottom of the column enriched NO₂ re-enters the rising hot stream where it is again dissociated into NO which undergoes further exchange with the descending stream of NO₂. In the cool region above the filament recombination of NO and O₂ occurs, yielding NO₂. Essentially, therefore, the gas in the system consists only of NO₂ except in the hot region where the decomposition into NO and O₂ is significant. The gases NO and NO₂ are readily interconvertible by a change in temperature. Thus a chemical converter which was necessary for the CO-CO₂ exchange is not required for the nitrogen exchange.

The data for an experiment at 0.5 atmos. is summarized in Table I. The isotopic abundances were measured to ±1.5 percent with a Nier type mass spectrometer. The NO₂ was reduced to N₂ by Fe powder at 400°C before isotopic analyses were made. The over-all separations shown in the table represent the ratio of the N¹⁵ abundance at the bottom of the column to that at the top.

Experiments at 0.25 atmos. and 1.0 atmos. gave values of 2.70 and 1.72, respectively, for the equilibrium separation. Calculation from the experiment at 0.5 atmos. gives a value of 1.1 cm for the H.E.T.P. using 1.006 for the equilibrium constant at 500°C.

Further study of this separation process is in progress.

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⁵ D. M. Yost and H. Russell, *Systematic Inorganic Chemistry* (Prentice-Hall Inc., New York, 1944), p. 29.