GEOMETRIC STRUCTURE AND VIBRATION FREQUENCIES OF $\text{Re}_2\text{F}_8$

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A complex electron diffraction and mass spectrometric investigation of the saturated vapor of rhenium tetrafluoride has been carried out. The principal molecular form in the vapor phase at $T = 471$ K is the dimer $\text{Re}_2\text{F}_8$. The geometric structure of the $\text{Re}_2\text{F}_8$ molecule has the equilibrium eclipsed conformation of symmetry $D_{4h}$ with a triple bond, $\text{Re} = \text{Re}$. The barrier to internal rotation of the $\text{ReF}_4$ groups relative to one another is $2.8 \pm 2.8$ kJ/mole. The vibration frequencies of the $\text{Re}_2\text{F}_8$ molecule have been estimated on the basis of the experimental amplitudes of vibration.

The structures of compounds of rhenium in low oxidation states are of special interest, particularly with respect to formation of rhenium–rhenium bonds. This paper is concerned with a structural investigation of the $\text{Re}_2\text{F}_8$ molecule which is the principal molecular form in the saturated vapor of rhenium tetrafluoride. The existence of this molecule was noted in papers [1, 2] concerned with a study of vaporization of Re(V) and Re(VI) fluorides by mass spectrometry. The authors [2] noted that rhenium did not form stable simple fluorides with an oxidation state less than four. They also noted that the monomeric molecule $\text{ReF}_4$ was absent from the gas phase of Re(IV) fluoride and that the large value of the enthalpy of dimerization of $\text{ReF}_4$ was a consequence of the strong $\text{Re} = \text{Re}$ bond in the $\text{Re}_2\text{F}_8$ molecule.

We have used electron diffraction coupled with mass spectrometric monitoring of the vapor phase composition to determine the geometric structure and vibration frequencies of the $\text{Re}_2\text{F}_8$.

EXPERIMENTAL

To choose the optimal conditions for the electron diffraction experiment we first carried out a study of the mass spectrum of $\text{ReF}_4$ at different temperatures. The results are presented in Fig. 1 as the intensities of the ion currents normalized to that of $\text{ReF}_3^+$. It can be seen that molecules of type (ReF$_3$)$_n$ (the ions ReF$_5^+$ and Re$_2$F$_9^+$ are representative) are present in the vapor phase along side molecules with the stereochemistry (ReF$_2$)$_n$. However, the relative intensities of the ions ReF$_5^+$ and Re$_2$F$_9^+$ decreased as the temperature increased and the fraction of these forms became small (1-3%) at $T = 468.5$ K. At the same time, the intensities of the ion currents for Re$_2$F$_7^+$ and Re$_2$F$_8^+$ remained high, which confirmed the previous conclusion [2] that the stability of the molecule Re$_2$F$_8$ was high. In these conditions it did not dissociate into the monomer. In this connection we to carry out the electron diffraction experiment at a temperature $T = 471$ K at which the dimer is the predominant form of rhenium tetrafluoride.

The electron diffraction plot of the saturate vapor above rhenium fluoride was obtained with an EMR-1130 machine [3, 4].

The starting material was synthesized by reduction of rhenium hexafluoride in a reactor with a spiral heated wire made of VR-20 alloy (20% Re, 80% W) by a method analogous to [5]. Optimum conditions for the synthesis of rhenium tetrafluoride were: diameter of the spiral 6 mm, pitch of the spiral 1-2 mm, temperature of the spiral 773 K, pressure (ReF$_6$) 10 mm.

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Fig. 1. Models of the geometric structure of the dimeric molecule of rhenium tetrafluoride.

by-product of the reduction, WF₆, was easily removed from the lower rhenium fluorides by vacuum distillation. Rhenium tetrafluoride was identified by chemical [6, 7] and x-ray phase analysis [8].

Vaporization was from a nickel ampul. The accelerating voltage was 75 kV (λ = 0.04326 Å) and the distances from the nozzle of the ampul to the photographic film were L₁ = 338.0 mm and L₂ = 598.0 mm.

A complete mass spectrum was recorded for each electron diffraction photograph. The mean diffraction intensity function Iₛ(s) was obtained from the latter with the following ranges of the diffraction angles: s₁ = 2.0-13.8 Å⁻¹ (L₁) and 5.2-26.0 Å⁻¹ (L₂). A graphic procedure was used to separate the reduced molecular components of the diffraction intensities sMₑₓᵖ(s).

STRUCTURAL ANALYSIS OF THE ELECTRON DIFFRACTION RESULTS

Assumption of the Simple Composition of the Vapor. Statistical Models of the Structure of the Re₂F₈ Molecule.

In the initial stage of the structural analysis it was assumed in constructing the theoretical analog of sM(s) that the vapor over rhenium tetrafluoride contained only the dimer molecules Re₂F₈. Because the structure of these molecules was unknown at that time, five possible models of the molecular structure were examined (Fig. 1):

1) a model with an eclipsed conformation of symmetry D₄h with an Re–Re bond (Fig. 1a);
2) a model with a staggered conformation of symmetry D₂d with an Re–Re bond (Fig. 1b);
3) a model with nonequivalent Re–F bonds and an Re–Re bond with symmetry D₂h (Fig. 1c);
4) a model with four Re–F₈ bridging bonds and symmetry D₂h (Fig. 1d); and
5) a model with an Re–Re bond and symmetry C₂h (Fig. 1e.).

The first two models were chosen by analogy with the structures of the [Re₂Cl₈]²⁻ ions in the crystals of Re₂Cl₅(dth)₂ [9] and [Re₂Br₈]²⁻ in crystalline Cs₂Re₂Br₅ [10] in which the intermolecular Re–Re distances may be somewhat shorter than in Re₂F₈ however because of the different multiplicities of the bonds. The configuration in the [Re₂Cl₈]²⁻ and [Re₂Br₈]²⁻ ions is σ²π⁴δ² while in the proposed Re₂F₈ molecule it is σ²π⁴. Moreover, the single δ bond in [Re₂Cl₈]²⁻ and [Re₂Br₈]²⁻ stabilizes the eclipsed conformation of the ions, while its absence in Re₂F₈ permits internal rotation of the ReF₄ units about the Re–Re bond which leads to the two possible structures: eclipsed (1) and staggered (2).