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Photochemical Decomposition of Nitryl Chloride

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It is the purpose of the present paper to verify the existence of step generation at edges of zinc whiskers. It is shown that the mechanism operates at very small undersaturations.

Zinc whiskers were grown in an apparatus that has been previously described.[8,9] The zinc metal was purified by triple distillation before being sealed into the growth vessel. The source zinc was held at 418°C. The ambient temperature surrounding the growth finger was 430°C. A stream of nitrogen was passed through the growth finger to lower its temperature to 415°C.

The growth process was observed at 25× with a Wild fixed-focus binocular microscope. In about 2 min, a crop of zinc whiskers grew to a length of 0.2–0.4 mm. Almost all of the whiskers executed a lively Brownian motion. The gas-flow rate was then slowly reduced until evidence of evaporation could be seen. Over a period of about 2 min the Brownian motion increased in intensity with an imperceptible change in length. The whiskers simultaneously became fainter and then disappeared.

In earlier experiments zinc whiskers a few microns in diameter were also observed to evaporate at constant length. They became thinner and less bright and disappeared with imperceptible change in length.

Whiskers[10–12] grow by the action of a single axial screw dislocation (or a coaxial group of screws). They only grow at supersaturations insufficient to give an inappreciable rate of two-dimensional nucleation. The screw growth mechanism[2] operates at very small supersaturations and only axial growth occurs.

It has been shown[11] that the average deflection of a whisker in Brownian motion can be used to estimate the whisker radius. The equation for the radius r of a whisker of circular cross section is

$$r=(8l^3kT/3\pi E\bar{\delta}^2)^{\frac{1}{4}}, \tag{1}$$

where l is the whisker length, k is Boltzmann's molecular gas constant, T is the absolute temperature, $\bar{\delta}$ is the average deflection of the whisker end, and E is Young's modulus for the whisker phase. The equation may be modified for differing whisker cross sections. For present purposes it is sufficient to use Eq. (1). Introducing numerical values $l=0.4$ mm, $\bar{\delta}=0.01$ mm, and $E=5\times10^{11}$ d/cm² it is found that

$$r=100\ \text{A}.$$

From Eq. (1) it is apparent that the Brownian motion must increase in intensity with decreasing whisker radius. For fixed length it is written

$$r=A\bar{\delta}^{-\frac{1}{2}}.$$

Deflections as large as 0.1 mm were observed before whisker disappearance, which corresponded to $r=30$ A.

It was clear that the disappearance of a whisker occurred almost solely by radial evaporation as contrasted to axial evaporation. From the whisker growth mechanism it was apparent that no screw dislocations were operating as growth sites in radial directions. Thus the evaporation occurred either by an edge source mechanism or by a two-dimensional nucleation of monolayer-holes.

The vapor pressure of zinc at 418°C is 0.14 mm Hg.[13] The zinc whiskers in Brownian motion evaporated radially at a rate of about 10^{-8} cm/sec, which corresponded to a pressure difference of about 10^{-6} mm between the vapor pressure of a whisker and the zinc pressure in the vapor phase. The undersaturation at which evaporation occurred was about $10^{-6}/0.1$ or 0.00001 at greatest. Since monolayer hole nucleation would require an understuration orders of magnitude larger, only the edge source of steps could operate. The evaporation behavior of whiskers of a few microns diameter was consistent with the behavior of the very small whiskers.

It must be concluded that the edges of zinc whiskers serve as step sources in agreement with the hypothesis of Hirth and Pound.[6] The mechanism operates at very tiny undersaturations. A second crystal is documented for which edge evaporation occurs.

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Photochemical Decomposition of Nitryl Chloride*

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THE mechanism for the thermal decomposition of nitryl chloride was suggested[1] to be the following:

$$NO_2Cl\rightarrow NO_2+Cl \qquad k_1, \tag{1}$$

$$NO_2Cl+Cl\rightarrow NO_2+Cl_2 \qquad k_2. \tag{2}$$

k_2 is presumed to be much larger than k_1. Cordes and Johnston[2] analyzed a number of reasonable variations and extensions of this mechanism, and concluded that Schumacher and Springer's original mechanism was very likely correct. A demonstration that chlorine atoms do indeed react rapidly with nitryl chloride would provide additional support for this mechanism; this was done as follows.

Nitryl chloride was prepared by the method of Wise and Volpe, as described by Volpe and Johnston.[3] Chemical analyses (as described by Volpe and Johnston) indicated a purity of the final product as 99±1%. Chlorine was removed from the crude product by vacuum distillation from a *n*-pentane slurry trap to a liquid nitrogen trap. Commercial chlorine, bromine, and nitrogen dioxide were used; the nitrogen dioxide was treated with oxygen to destroy N_2O_3. All were purified by vacuum distillation.

The apparatus was a conventional vacuum line. Photolyses were carried out in an air-thermostatted 500-ml Pyrex bulb; a Hanovia SH mercury arc and a heat-absorbing filter was used. The reaction was followed by measuring the pressure increase as a function of time with a Bourdon gauge and manometer system. Fluorocarbon stopcock grease (Ascolube F) was used throughout.

An induction period was found when pure nitryl chloride vapor was used. The plot of pressure vs time remained nearly flat for approximately 5 to 10 min; then curved upward and after an additional 2 to 3 min became linear with slopes of approximately 1.2 mm Hg/min at 78°C, using full light intensity. The slopes of the linear portions of the curves were directly proportional to the incident light intensity and independent of nitryl chloride pressure. A rough calculation of an activation energy yields 0–2 kcal; due to variations in the intensity of the light source we were unable to obtain more precise results. Initial nitryl chloride pressure was varied from 50 to 200 mm Hg. Products were chlorine and nitrogen dioxide. After several runs had gone to completion, the products were frozen out with liquid nitrogen. Negligible amounts of noncondensible gas were produced, indicating the absence of oxygen. Vacuum distillation yielded the calculated amount of chlorine. The color of nitrosyl chloride was not observed in the liquid nitrogen exhaust traps.

The addition of chlorine to the nitryl chloride vapor completely eliminated the induction period if the chlorine partial pressure was 10 mm Hg or more; bromine vapor and nitrogen dioxide also eliminated the induction period. It is presumed that the occurrence of any photochemical reaction at all in "pure" nitryl chloride is due to the presence of traces of sensitizing impurity, probably chlorine.

Our observations can be accounted for by the following simple mechanism:

$$\mathrm{Cl_2} \rightarrow 2\mathrm{Cl} \qquad (3)$$

$$\mathrm{Cl}+\mathrm{Cl}+\mathrm{M} \rightarrow \mathrm{Cl_2}+\mathrm{M} \qquad k_4 \qquad (4)$$

$$\mathrm{Cl}+\mathrm{NO_2Cl} \rightarrow \mathrm{NO_2}+\mathrm{Cl_2} \qquad k_2. \qquad (5)$$

If one makes the steady-state assumption for [Cl], and further assumes that $I\cdot k_4\cdot[\mathrm{M}]\ll k_2{}^2\cdot[\mathrm{NO_2Cl}]^2$, one finds that the rate of the reaction should be proportional to the amount of light absorbed and independent of everything else, as is observed. Bromine molecules might well be expected to sensitize the reaction in a way similar to chlorine. Electronically excited nitrogen dioxide molecules could also readily supply the 29.5 kcal required to break the N—Cl bond.

In conclusion, our photochemical results appear to confirm the accepted mechanism for the thermal decomposition of nitryl chloride.

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Heats of Hydrogenation as a Function of Hybridization

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IN recent years there has been a growing tendency to explain the properties of molecules in terms of hybridization instead of resonance. Noteworthy among the leaders of this movement is M.J.S. Dewar. His position has been that some of the variations in the physical properties as well as thermodynamic properties are more easily interpreted in terms of hybridization rather than resonance.[1,2] The idea that bond lengths are a function of hybridization is not original with Dewar, but was proposed some years ago by Walsh,[3] Coulson,[4] and more recently by Brown,[5] and Somayajulu.[6] Dewar has also applied the concept of hybridization to explaining the variations in thermodynamic properties, but not with the high degree of success that it was applied to bond lengths.[2] Unfortunately, Dewar uses the term "stabilization energies," which still leaves something to be explained. Dewar also considers only the contributions made by variations in the hybridization of carbon-carbon bonds without further extending the concept to carbon-hydrogen bonds. This necessitates the introduction of further parameters such as the bond energies for primary, secondary, and tertiary carbon-hydrogen bonds. The purpose of this work is to show that there is a high degree of correlation between hybridization and the heats of hydrogenation as Dewar has suggested.

In addition to the carbon-carbon double bond, ethylene also consists of four hydrogen-carbon (sp^2)