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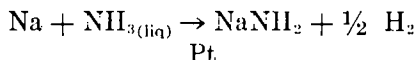
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## Heterogeneous Catalysis of a Dilute Solution of Sodium in Liquid Ammonia

### INTRODUCTION

It is well known that platinum catalyzes the decomposition of alkali metal solutions in liquid ammonia (1, 2). The purpose of this note is both to present some quantitative data on the reaction



at  $-78^\circ\text{C}$  and to consider the effect of initial treatment of this system on the rate of decomposition. Because the initial treatment significantly alters the rate of decomposition of metal-ammonia solutions, it is necessary to consider the initial purification of the glass surface prior to its contact with the blue solution (3, 4).

### EXPERIMENTAL

A simple procedure for the preparation of a dilute solution of sodium in liquid ammonia at  $-78^\circ\text{C}$  has been described previously (5). This procedure was used to wash the surface of the ampule including a platinum foil ( $4.3 \times 2.5 \times 0.015$  cm) for varying lengths of time. After washing the system with the blue solution, the ammonia was distilled into another ampule on the vacuum line. Then the system was flamed (while pumping) to distill out any volatile residue. The above procedure was repeated to prepare 4.0 cc of the sodium-ammonia solution at  $-78^\circ\text{C}$ , and its de-

composition was studied in the presence of the platinum foil. Pressure measurements of the evolved hydrogen were made by means of a calibrated McLeod gauge, which had a trap with a liquid nitrogen bath around it between the McLeod gauge and the ampule containing the blue solution. (The volume of the system was 1.74 liters.) At convenient time intervals the pressure of the evolved hydrogen was measured by replacing the dry ice-acetone bath with a liquid nitrogen bath. After each pressure measurement, the evolved hydrogen gas was pumped out of the system. When the final pressure measurement of each "run" was made, the blue coloration had completely faded. The initial concentration of sodium was calculated from the total pressure of evolved hydrogen (at room temperature) (Fig. 1).

### RESULTS AND DISCUSSION

Figure 1 summarizes the kinetic data, including the effect of washing the system with the blue solution at  $-78^\circ\text{C}$ . The data plotted (pressure vs. time) seem to indicate that two reactions occur: (1) reaction at the glass-liquid interface due to the presence of adsorbed water (5), (2) reaction at the platinum-liquid interface (1). The effect of washing the system with a blue solution for increasing lengths of time appears to be a decrease in the evolution of hydrogen in the first reaction. This trend is to be expected if adsorbed water is

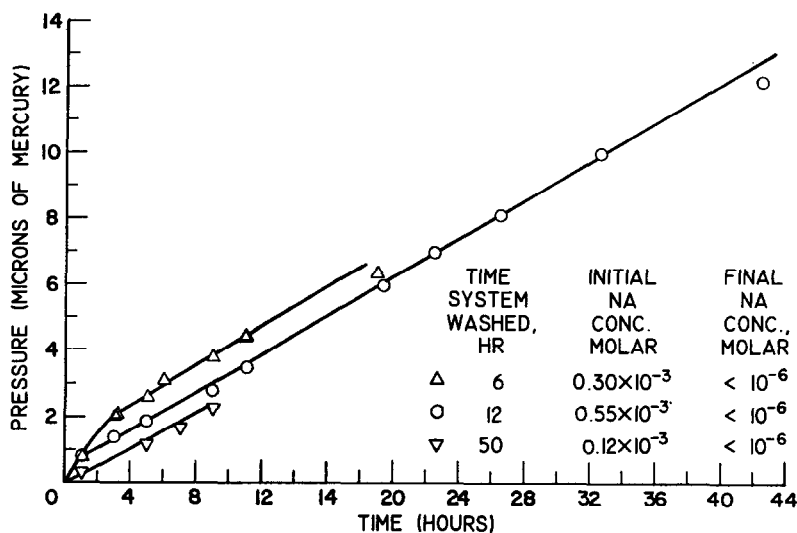


FIG. 1.

initially present at the glass-liquid interface at  $-78^{\circ}\text{C}$ . After washing for 50 hr, the first reaction no longer occurs (and the second reaction is zero order). The rate constant for the decomposition of dilute solutions of sodium in liquid ammonia  $< 10^{-3} M$  at the platinum-liquid interface is  $0.33 \pm 0.03$  micron of Hg/hr (corrected for presence of liq  $\text{N}_2$  bath) or  $1.5 \pm 0.15 \times 10^{-9}$  moles of  $\text{H}_2/\text{cm}^2\text{hr}$  at  $-78^{\circ}\text{C}$ .

Efforts to obtain reproducible results without washing the metal-glass system with a blue solution were unsuccessful. After the rate of hydrogen evolution had decreased for the unwashed system, the reaction became zero order, but the slope varied from 0.15 to 0.50 micron of Hg/hr. This was nonreproducible from experiment to experiment. Apparently the initial treatment of the system is critical in obtaining a reproducible slope. An examination of the data shown in Fig. 1 indicates that for a tenfold decrease in concentration of sodium accompanied by a corresponding increase in the concentration of sodium amide, the slope remains constant. This suggests that the sodium amide does not alter the rate of decomposition. This conclusion is in agreement with the observations made previously for the platinum-potassium-ammonia system at  $-33^{\circ}\text{C}$  (1). Here, Burgess and Kahler found that potassium amide does

not alter the rate of decomposition of the above system. However, for the platinum-sodium-ammonia system at  $-33^{\circ}\text{C}$ , they report that the system decomposes in a nonreproducible manner from experiment to experiment. They attribute this nonreproducibility to poisoning of the platinum surface by sodium amide.

However, it is not necessary to conclude that poisoning of the platinum surface by  $\text{NaNH}_2$  will lead to nonreproducibility of the kinetics of decomposition. For example, if it is assumed that poisoning of the platinum surface begins during the initial precipitation of  $\text{NaNH}_2$ , then it is possible to calculate the amide concentration necessary for this to occur from the initial sodium concentration using the relationship  $[\text{Na}^+][\text{NH}_2^-] = K_{SP}$  (where concentrations are used in place of activities). During the decomposition of the blue solution, the amide concentration increases until  $[\text{NH}_2^-] > K_{SP}/[\text{Na}^+]$ , whereupon the rate of decomposition is altered by poisoning of the catalyst by precipitation of sodium amide. Thus, in different experiments, despite poisoning of the platinum surface, the rate of decomposition could be determined in a reproducible manner from the initial sodium concentration. It seems more likely that the observed nonreproducibility is associated with the initial presence of

adsorbed water on the catalyst surface (3, 5).

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## Effect of Sorbed Oxygen and Carbon Monoxide on the ESR of Zinc Oxide

We wish to report exploratory electron spin resonance (ESR) measurements which show that the interaction of oxygen and carbon monoxide with a zinc oxide catalyst can be studied by varying the gas phase. The observed resonance changes are tentatively interpreted in terms of the formation of sorbed paramagnetic species and changes in the electronic properties of the solid. In addition, we believe that our experiments suggest the possibility of determining the distribution of certain solid-state defects between the bulk and the surface of the solid.

The ZnO (S.P. 500, New Jersey Zinc Company) sample was mounted in a conventional high vacuum system. For the pretreatment heating procedure the portion of the stationary vacuum system containing the sample was surrounded by a movable furnace. Without opening the vacuum system the furnace could be replaced by the ESR cavity. The ESR measurements and the exposure of ZnO to ambient atmospheres were all made at room temperature. The Varian V-4502 spectrometer was operated at 9380 Mc/sec with a dual cavity and a 12-inch magnet. The multipurpose sample cavity employed 100 kc field modulation; the reference cavity employed 400 cps field modulation and was equipped

with a standardized pitch sample for the calibration of instrumental sensitivity and gyromagnetic ratio ( $g$ ) or with a  $10^{-2} M$   $MnSO_4$  solution for the determination of the magnetic field dispersion. The absolute values of  $g$  were determined to within  $\pm 0.1\%$ . The ESR measurements shown in Fig. 1 were made using a power level of 44 mwatts, at which power saturation effects, present for the  $g = 2.004$  line but not for the  $g = 1.96$  line, were shown not to account for the differences produced by varying the gas phase from vacuum to oxygen. The relative ESR signal heights were determined from the peak-to-peak heights of the derivative curves and were normalized for instrumental gain; all other ESR instrumental parameters were held fixed. The signal height was assumed to be proportional to the number of spins, since the line width remained sufficiently constant.

Figure 1 shows the effect on one sample of ZnO of a sequence of ambient atmospheres on the relative signal heights of three resonance signals measured as a function of time after pretreatment. The complete sequence of ambient gas exposures following pretreatment was carried out on five samples. The direction of the signal height change, i.e., increase, decrease, or no