The Role of Starting Voltage in the Kinetics of Decomposition of Ammonia under Electric Discharge

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The decomposition of ammonia by second order kinetics in a wire to cylinder type electric discharge has been studied at different initial pressures in the range of 50 – 200 mm Hg at various applied voltages and various discharge currents. Even though the initial pressures are different, yet, in every case the application of the same multiple of the respective starting voltage ensures that the decomposition occurs with the same specific rate.

In a gas phase reaction in an electric discharge the reaction rate depends largely on the discharge current[1, 2]. Our study concerns the criterion which ensures that a reaction in a certain discharge tube occurs at the same specific rate even when the gas is at different initial pressures. In an earlier communication[3] it was shown that the first order decomposition of nitrous oxide under electrodeless discharge at different initial pressures occurs at the same specific rate when the same multiple of the respective starting voltage was applied. Since that study was of limited scope, the criterion was not claimed to be universally applicable. An investigation with another gas, decomposing with a different kinetic order, in a discharge tube of a different type would enable a wider applicability of this criterion to be tested. Therefore, in the present work the decomposition of ammonia occurring by second order kinetics in a wire to cylinder type discharge has been studied. Several investigators[4–6] have studied this decomposition with respect to its kinetics, formation of intermediates, influence of added gases on the rate, etc. The present study, however, is solely concerned with the criterion mentioned above.

The discharge tube consists of a 10 cm long, 2 cm wide glass tube closed at both ends, at the axis of which a tungsten wire W (0.5 mm diam) is stretched (Fig. 1). An aluminium foil A is wrapped tightly on the outer surface of the tube. Electric discharge is excited by applying a.c. (50 Hz) voltage from a high voltage transformer HT at the tungsten wire and the aluminium foil. Any desired voltage can be applied by controlled input to the transformer HT from a variable voltage transformer VT. The discharge current is measured by a microammeter μA in the in the circuit.

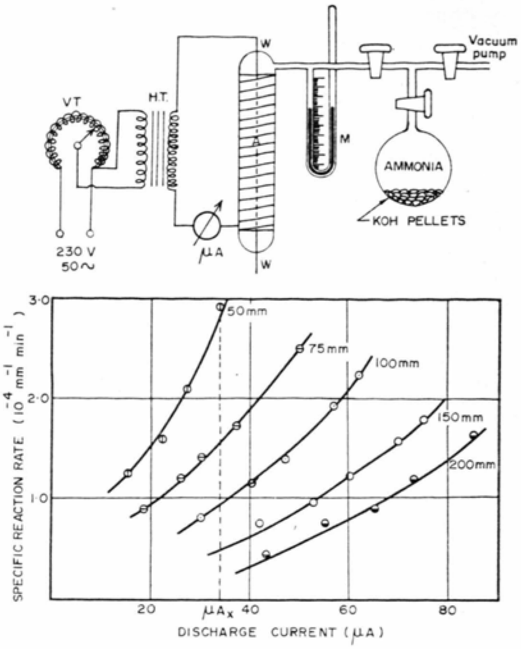

Fig. 1. Above: Schematic diagram of experimental set up. Below: Variation of specific rate with discharge current.

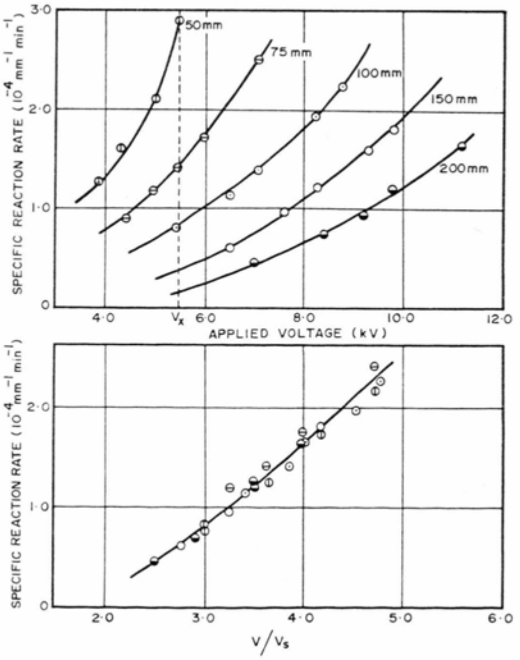

Fig. 2. Above: Variation of specific rate with applied voltage. Below: Variation of specific rate with multiple of respective starting voltages.

The discharge tube is evacuated and filled with ammonia at a pressure p_0 at 25 °C. The voltage V_s at which the electric discharge just starts is noted and a higher voltage V is applied. The total pressure p as well as the discharge current μA are noted at intervals of time. The discharge current remains fairly constant throughout the decomposition. The power input to the discharge tube is less than 1 watt and there is no observable temperature rise in it. The second order specific rate of the decomposition is evaluated from the slope of the linear curve obtained by plotting $1/(2\,p_0-p)$ versus time.

The decomposition is studied at five different applied voltages with five different pressures of ammonia. At each pressure the specific rates are plotted separately versus the discharge current, applied voltage and multiple of the starting voltige, V/V_s. The results are presented in Figures 1 and 2.

The range of initial pressures over which the kinetics has been studied is limited to 50 – 200 mm Hg due to experimental difficulties. Yet the curves for specific rate versus discharge current or versus applied voltage are distinctly different for the various initial pressures. Further, the specific reaction rates are also widely different even though the same discharge current μA_x or the same voltage V_x be applied in every case. As compared with these, when the specific rates are plotted versus the multiple of the starting voltage, all the twenty five points fall on a single curve and the various initial pressures become indistinguishable. The slight scattering of the points around the curve is due to experimental errors in the kinetic measurements. This clearly shows that even though the initial pressures are different, the application of the same multiple of the respective starting voltage ensures the same specific rate.

In comparison with the decomposition of nitrous oxide by first order kinetics under electrodeless discharge[3], in the present study the gas is different, the kinetic order of decomposition is different and the type of electric discharge is different, yet the conclusion regarding the criterion to ensure the same specific reaction rate when the gas is at different initial pressures, is the same.

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Berichtigungen

Zu M. Mehring, Arbitrary Pulse Width in the Four-Pulse NMR-Experiment, Z. Naturforsch. **27 a,** 1634 [1972].

This is to correct some printing errors in the above mentioned article.

Equation (3c) should read: $\widetilde{\mathcal{H}}(t) = L_1^{-1}(t)\,\mathcal{H}_{\text{int}}\,L_1(t)$.
Equation (16 a) should read:

$$D_0 = \frac{3}{2}\cos\beta_1\left[\frac{k(1-\delta)}{1+k}\cos\beta_1 + \delta\,\frac{\sin\beta_1}{2\,\beta_1}\right] + \frac{1+(1-k)\,\mathbf{(}1-(3/2)\,\delta\mathbf{)}}{2\cdot(1+k)}\,.$$

In Eq. (20 a) and Eq. (20 b) a δ is missing in front of the expression $\sin\beta_1/\beta_1$.
Thus $\sin\beta_1/\beta_1$ in both equations has to be replaced by: $\delta(\sin\beta_1/\beta_1)$.

In Eq. (20 d) the term $\frac{3}{2}\,(1-\frac{3}{2}\,\delta)$ has to be replaced by: $\frac{1}{3}\;(1-\frac{3}{2}\,\delta)$.

Zu E. Engel, P. John und B. Reuse, Messungen von Lebensdauern für den Fall untrennbarer Energien der $\gamma-\gamma$-Kaskade, Z. Naturforsch. **27 a,** 1368 [1972].

Formel (2) muß richtig heißen:

$$\frac{\mathrm{d}\ln F(x)}{\mathrm{d}x} = -\frac{1}{\tau}\left[1-\frac{P(x)}{F(x)}\right]. \tag{2}$$

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