# The Role of Starting Potential in the Kinetics of Chemical Reactions under Electrodeless Discharge

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It has been shown that in kinetically first order gas phase reactions occuring under electric discharge, such as the decomposition of $N_2O$, the application, at various initial pressures, of the same multiple of the respective starting potential ensures that the reaction occurs at the same specific rate.

Several investigations of chemical reactions under electric discharge emphasize a close parallelism between the discharge current and the rate of the reaction. This has been expressed by the equation $dp/dt = \alpha I$ where $p$ is the pressure, $I$ the discharge current and $\alpha$ a constant[1–4]. These reactions are, therefore, kinetically of zero order. However, there are some instances in which, at constant applied potential, the reaction is of the first order. In such instances the question arises which potential has to be applied for various initial pressures in order to bring about the same specific reaction rate.

The reaction chosen in this study is the decomposition of nitrous oxide under electrodeless discharge which has been shown to be of the first order[5, 6]. The absence of metal electrodes in the system eliminates the possibility of any catalytic effects. Nitrous oxide of purity 99.5% is used. The discharge tube is a Siemens' type all glass ozonizer, 25 cm long and with 5 mm annular width. It can be evacuated and filled with nitrous oxide at any desired pressure.

The electrical discharge is excited at 50 Hz by a step up transformer. Any desired potential can be applied to the discharge tube by controlled input to the step up transformer. The current through the discharge tube is measured by an a. c. microammeter of the rectifier type.

The decomposition is studied for several initial gas pressures ($p_0$) in the range $20-100$ Torr and at various exciting potentials (V). At the commencement of each trial the starting potential and the discharge current (I) are noted. The total pressure $P$ is measured at intervals of time, keeping the temperature and the volume constant. Since nitrous oxide decompose according to the stoichiometric equation

$$N_2O = N_2 + \tfrac{1}{2} O_2$$

the partial pressure $p_{N_2O}$ is given by the expression

$$p_{N_2O} = p_0 - 2(P - p_0).$$

The specific reaction rate is evaluated from the slope of the log $p_{N_2O}$ vs. time curve.

Typical results for the initial pressures of 20, 50, and 100 Torr are presented in Fig. 1, which shows the decomposition (a) at constant potential (3.3 kV) and (b) at 1.5 times the respective starting potential.

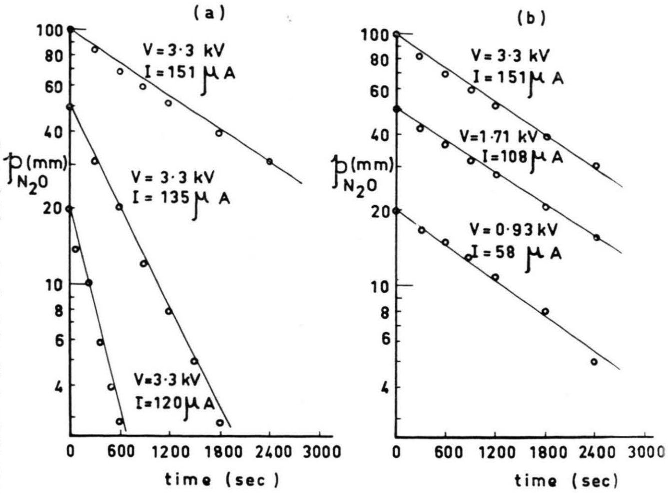

Fig. 1. Decomposition of nitrous oxide under electrodeless discharge: (a) at 3.3 kV, (b) at 1.5 times the respective starting potential.

Fig. 1 (a) shows that even though the applied potential is the same for the three initial pressures 20, 50 and 100 Torr, the decomposition occurs at widely different specific rates, namely $3.04 \times 10^{-3}$ sec$^{-1}$, $1.13 \times 10^{-3}$ sec$^{-1}$ and $0.50 \times 10^{-3}$ sec$^{-1}$ respectively. Such a wide difference in the specific rates occurs even though the initial discharge currents in these cases are of comparable magnitudes, namely, 120 μA, 135 μA and 151 μA respectively. It can therefore be inferred that bringing about the decomposition at the same discharge current also would not ensure the reaction to occur at the same specific rate. As compared to these, Fig. 1 (b) shows that when the potential applied in each case is 1.5 times the respective starting potential, the specific rates are almost the same, namely $0.52 \times 10^{-3}$ sec$^{-1}$, $0.48 \times 10^{-3}$ sec$^{-1}$ and $0.50 \times 10^{-3}$ sec$^{-1}$ respectively. The discrepancies in the three values are mostly due to experimental errors. Evidently, the absolute magnitudes of the potentials as well as the initial discharge currents are all different in the three cases. From this it appears that within the limits of the reaction being of the first order, if the same multiple of the respective starting potential is applied to the gas at different initial pressures, the reaction occurs at the same specific rate in every case.

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