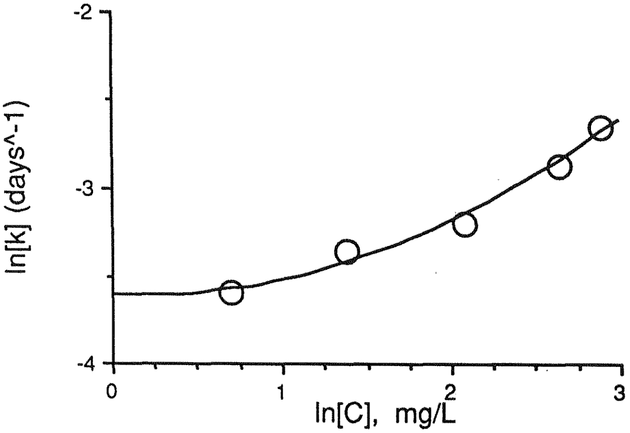

Fig. 7 Effect of oxygen concentration on oxidation rate. If plotted linearly the equation for the trace would be $y = -3.93 + 0.41x$. It is shown parabolically: $y = -3.6 - 0.04x + 0.125x^2$. (Figure constructed from data by Kassem, 1972.)

oxidation of ascorbic acid (Kassem et al., 1972) (where, however, the slope is not unity).

1.5. Oxidative Autocatalysis

In autocatalysis, the rate constant, k_2, is a function of Y. The most all-encompassing equation of this type is the Ng equation, Eq. (4.43) (Ng, 1975) which will be dealt with at another point. Eq. (4.23) assumed that the reaction rate was proportional to drug concentration and reactant concentration. Where this is in deviance from experimental results it may be assumed that it is dependent on powers of these, i.e.,

$$\frac{dY}{dt} = k_2 Y^n (1 - Y)^p \tag{4.43}$$

In many cases, the exponents are simply unity, and hence Eq. (4.43) becomes

$$\frac{dY}{dt} = k_2 \cdot Y[1 - Y] \tag{4.44}$$

where, here, Y denotes fraction decomposed. Profiles of this type are shown in Fig. 8.

There is an initial apparent lag time, and then a precipitous drop. Often, in real systems, it is difficult to duplicate the induction time point, t^*, at which the drop commences. The FDA has often quoted this situation as one that makes the Agency leery about extrapolations, because it is possible to get a good linear fit to the data at times $t < t^*$, and these would extrapolate to high retention values, which in the case cited would be incorrect. Eq. (4.44) is rearranged to

$$\frac{dY}{Y(1 - Y)} = k_2 t \tag{4.45}$$