



**Fig. 5** Photolytic oxidation of ascorbic acid solutions. Least squares fit: 10 mg% methionine:  $y = 99.38 - 7.64x$  ( $R = 0.97$ ) and no methionine:  $y = 104.19 - 4.67x$  ( $R = 0.95$ ). (Graph constructed from data by Asker et al., 1985.)

1995). These are cases where the drug is amphiphilic and where one of the non-micellar  $n$ -mers ( $A_n$ ) oxidizes. In this case there is an excess of oxygen, and the concentration of the reaction species,  $A_n$ , is constant (since it will be replenished by the micellar species).

Cases where the oxidation is photochemically driven will often become zero order. An example of this is the work by Asker et al. (1985), whose data are shown in Fig. 5. It should be noted that the data are probably more suitably considered S-shaped curves, such as will be discussed shortly.

#### 1.4. Oxidation in an Open System

It is always worthwhile determining  $k_2$  in a separate experiment in an open system. This is done by bubbling oxygen through an aqueous solution of drug, so that  $C$  is the saturation concentration of oxygen ( $C_{\text{sat}}$ ) at all times:

$$\frac{dA}{dt} = -k_2[A]C_{\text{sat}} = -k_2[A]KP \quad (4.37)$$

Since the amount of A present is the original amount of drug,  $A_0$ , less the amount decomposed,  $Y^*$ , it follows that

$$\frac{dY^*}{dt} = k_2[A_0 - Y^*]KP \quad (4.38)$$

It is noted here that the  $A^*$  and  $Y^*$  values are  $V_2$  times concentrations. Eq. (4.40) integrates to

$$\ln[A^* - Y^*] = -(k_2KP)t + \ln[A_0^*] \quad (4.39)$$