Inorganica Chimica Acta, 23 (1977) L31–L32

Rate Constants of the Permanganate Oxidation of Dimethylmaleic Acid and Dimethylmaleic Anhydride

Z. SZEVERENYI, L. I. SIMANDI* and M. JAKY

Central Research Institute for Chemistry, Hungarian Academy of Sciences, H-1025 Budapest, Pusztaszeri ut 59/67, Hungary

Received April 17, 1977

The kinetics of the permanganate oxidation of dimethylmaleic acid (H_2A) have been studied by the stopped-flow technique in acidic solutions [1]. The reaction has been found to obey the kinetic equation

$$-d[MnO_4^-]/dt = k[H_2A]_T[MnO_4^-] \qquad (1)$$

where $[H_2A]_T$ is the overall concentration of dimethylmaleic acid. The observed second-order rate constant k depends on the pH, owing to the different reactivities of the species H_2A, HA^- and A^{2-} characterized by rate constants k_1, k_2 and k_3, respectively. As the solutions used in the kinetic runs were prepared by acidification of a strongly alkaline stock solution, dimethylmaleic anhydride was thought to be absent in the reacting solutions. This assumption is unfounded and leads to an incorrect value for k_1 [1] as the equilibrium between the diacid and the corresponding anhydride is established rather rapidly [2]. In this communication, we report a kinetic study that yields both the correct value for k_1 and the rate constant of the permanganate oxidation of dimethylmaleic anhydride.

According to a detailed study by Eberson [2], the equilibrium constant for the formation of dimethylmaleic anhydride (DMA)

$$H_2A \underset{k_{-a}}{\overset{k_a}{\rightleftharpoons}} DMA + H_2O \qquad (2)$$

$K = k_a/k_{-a} = 5.3$ at 20 °C in water; the values of the rate constants are $k_a = 1.07\ min^{-1}$ and $k_{-a} = 0.204\ min^{-1}$ irrespective of the hydrogen ion concentration. Although reaction (2) is rather fast in both directions (half-time of equilibration 0.55 min), its rate remains much below that of the permanganate oxidation of either species, which occurs with a half-life of a few seconds. Therefore, if an equilibrated solution containing both H_2A and DMA reacts with MnO_4^-, the more reactive species will be consumed more rapidly and the equilibrium distribution will be perturbed by the oxidation. Consequently, the usual assumption [1, 3] of fast equilibration between the reactant species (*e.g.* diacid and its anions) is not valid if the anhydride is also present. This requires a different approach for obtaining correct rate constants for the permanganate oxidation of H_2A and DMA, k_1 and k_0, respectively.

Preliminary estimates indicate that k_0 is much greater than k_1, which precludes the precise evaluation of both rate constants from kinetic runs performed with an equilibrated solution. Under such conditions DMA predominates (about 85%) and the contribution of the remaining 15% H_2A to the rate is very nearly negligible. It would be preferable to carry out the kinetic measurements with a solution containing mainly the diacid.

In alkaline solutions, dimethylmaleic acid is fully converted to the dianion, pK_2 being equal to 6.1 [2]. Upon acidification in the stopped-flow mixing chamber within a few msec, very fast protonation of the carboxylate groups will yield a solution containing practically 100% H_2A. If the acid solution used also contains MnO_4^-, then the kinetic trace of oxidation can be immediately recorded for a non-equilibrium system in which the diacid predominates. Although equilibration is significantly slower than oxidation (both are much slower than the protonation of A^{2-}), the kinetic treatment cannot be simplified. The concentration of DMA, the more reactive species, gradually increases from zero to about 7% during a run, therefore no pseudo-first order conditions can be ensured. This requires that the rate constants be evaluated by considering the full reaction scheme as given by eqn. (3)–(5):

$$H_2A \underset{k_{-a}}{\overset{k_a}{\rightleftharpoons}} DMA \qquad (3)$$

$$H_2A + MnO_4^- \xrightarrow{k_1} X_1 \qquad (4)$$

$$DMA + MnO_4^- \xrightarrow{k_0} X_0 \qquad (5)$$

(here X_1 and X_0 are cyclic hypomanganate esters [1], which rapidly decompose in a subsequent step). The time-dependence of the concentrations involved is governed by the following system of differential equations:

$$d[H_2A]/dt = = k_{-a}[DMA] - k_a[H_2A] - k_1[H_2A][MnO_4^-] \qquad (6)$$

$$d[DMA]/dt = = -k_{-a}[DMA] + k_a[H_2A] - k_0[DMA][MnO_4^-] \qquad (7)$$

$$d[MnO_4^-]/dt = -(k_1[H_2A] + k_0[DMA])[MnO_4^-] \qquad (8)$$

which cannot be integrated in an exact form. Con-

---

*To whom correspondence should be addressed.

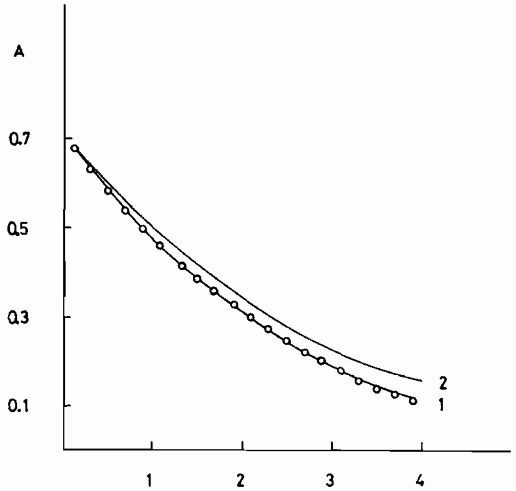

Fig. 1. Typical absorbance *vs.* time curve (solid line 1) for the permanganate oxidation of dimethylmaleic acid produced by acidification of an alkaline solution in the stopped-flow mixing chamber. The points were calculated with the best-fit rate constants. Curve 2 was calculated with the best k_1 neglecting anhydride formation. Conditions: $[MnO_4^-]_0 = 1.5 \times 10^{-3}$ *M*; $[H_2A]_T = 1.5 \times 10^{-2}$ *M*; $[HClO_4] = 0.1$ *M*. Wavelength 540 nm, optical path 0.2 cm, T = 20 °C.

sequently, no expression can be obtained for the stopped-flow traces recorded, *i.e.* for the $[MnO_4^-]$ *vs.* time relationship.

For evaluation of the unknown rate constants k_0 and k_1 a computer program has been devised, in which numerical integration is combined with parameter optimization. In order to fit eqs. (6)–(8) to the experimental stopped-flow traces, k_0 and k_1 were let to vary according to a gradient type routine and the change in error after each step was calculated by comparing the trace with the curve obtained by numerical integration using the last values of the two rate constants. Integration was performed by a routine based on Adams' predictor–corrector method. These two cycles were repeated until the difference between the experimental and calculated traces reached a minimum. This approach is generally suitable for kinetic systems where exact integration and fitting of the resulting expression to the data is not feasible.

Application of the above procedure yielded $k_0 = 250 \pm 20$ dm³/mol s and $k_1 = 25.5 \pm 2.5$ dm³/mol s at 20 °C in water. The fit achieved is illustrated by Fig. 1, where the points are calculated and the solid line is the experimental stopped-flow trace. For comparison, the curve calculated for step (4) as the only reaction is also shown, demonstrating the necessity of a neglect-free treatment.

A pseudo-first order approximation for the evaluation of k_0 from traces for equilibrated anhydride/H_2A solutions (k_1 term neglected) yields $k_0 = 240 \pm 20$ dm³/mol s, in reasonable agreement with the refined result.

The correct values now available for k_0 and k_1 are in line with the general trend that the monoanions of various maleic acid derivatives are more reactive toward MnO_4^- than both the undissociated acid and the dianion [1, 3]. This is attributed to the planar structure of these species imposed by strong hydrogen bonding. The planar structure is even more rigid in the anhydride, which explains why its reactivity exceeds that of the monoanion ($k_2 = 90$ dm³/mol s) [1].

References

1 M. Jáky and L. I. Simándi, *J. Chem. Soc. Perkin II,* 939 (1976).
2 L. Eberson, *Acta Chem. Scand., 18,* 1276 (1964).
3 L. I. Simándi and M. Jáky, *J. Chem. Soc. Perkin II,* 1856 (1973).