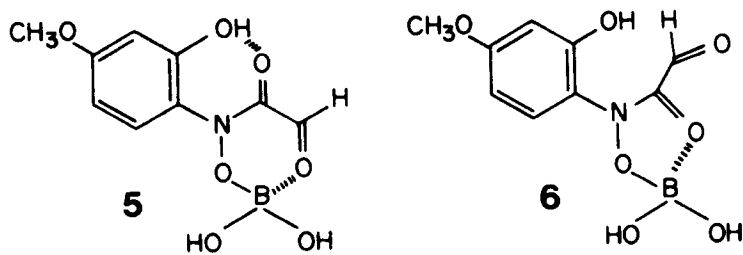


Fig. 1. Effect of borate (○) and phosphate (●) pH 9 on the rate of decomposition of DIMBOA (8×10^{-5} M) at 31° .

Fig. 2. Absorption spectra of 8×10^{-5} M solutions of compounds 1, 3 and 4 in 0.1 M phosphate (---) and borate (---) pH 9 buffers.

Fig. 2 shows that while the optical density of 4 at 260 nm substantially increased in borate as compared with phosphate buffer, the absorption peaks of 1 and 3 at 290 and 300 nm respectively, were not affected. These results indicate that only compound 4 interacts with borate, and give support to the proposal of complex formation between the open-chain form of DIMBOA, 2, and borate. This complex was not detected in the spectrum of DIMBOA presumably due to the low equilibrium concentration of 2.¹²

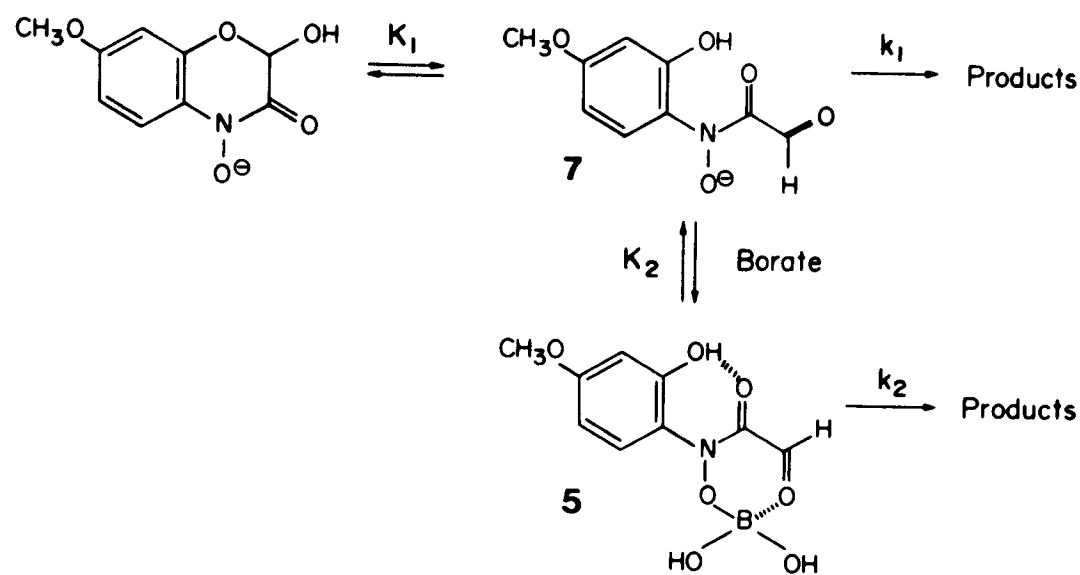
The structure of the complex can not be similar to that reported for other hydroxamic acids,⁹ since no enolizable hydrogen is present in 2. However, analogous interaction of borate with the hydroxamic hydroxyl moiety leads to structures 5 and 6. From a thermodynamic viewpoint, complex 5 would be favored



since it involves the formation of a 6-membered ring and is further stabilized by intramolecular hydrogen bonding.

The fact that cyclic hydroxamic acids 1 and 3 do not show interaction with borate, may be rationalized on the basis of interatomic distances. The distance between the hydroxamic hydroxyl oxygen and the carbonyl oxygen has been determined crystallographically as 2.84 Å in the analogue of DIMBOA lacking the 7-methoxy group.¹³ This distance is 0.49 Å longer than the O-O distance in boric acid. Thus, the formation of a complex of type 6 is less likely on this basis, and also because it would necessarily lead to a 5-membered ring.

The following scheme is hence postulated for the decomposition of DIMBOA in the presence of borate pH 9:



Under steady-state conditions, equation 1 is obtained.¹⁴ This may be reduced to equation 2, in which k_{obs} and k°_{obs} are the observed rate constants in the

$$v = \frac{K_1}{1 + K_1} (\text{DIMBOA}) [k_1 + k_2 K_2 (\text{Borate})] \quad (1)$$

$$\frac{v}{(\text{DIMBOA})} = k_{\text{obs}} = k^{\circ}_{\text{obs}} + k_{\text{cat}} (\text{Borate}) \quad (2)$$

presence and absence of borate. This model fits the experimental results shown in Fig. 1, with a catalytic constant, k_{cat} , equal to $0.103 \text{ min}^{-1} \text{ M}^{-1}$.

The formation of products from intermediate 2 (or 5) involve the nucleophilic attack of the hydroxamic oxygen atom on the aldehydic carbonyl group.^{10,11} The catalytic effect of borate may arise from both thermodynamic and kinetic factors. Since an open-chain intermediate is necessary for reaction, the

displacement of equilibria towards this compound via formation of borate complex 5 favors the reaction. On the other hand, complex 5 is presumably more reactive than 7 on entropic grounds (reactive groups are held in suitable position for reaction) as well as on enthalpic grounds (strong polarization by boron of the aldehydic carbonyl group).

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REFERENCES AND NOTE

- 1 V.H. Argandoña, L.J. Corcuera, H.M. Niemeyer and B.C. Campbell, Ent. Exper. Appl., 1983, **34**, 134.
- 2 B.J. Long, G.M. Dunn, J.S. Bowman and D.G. Routley, Crop Sci., 1977, **17**, 58.
- 3 L.J. Corcuera, M.D. Woodward, J.P. Helgeson, A. Kelman and C.D. Upper, Plant Physiol., 1978, **61**, 791.
- 4 B.J. Long, G.M. Dunn and D.G. Routley, Crop Sci., 1978, **18**, 573.
- 5 Y. Hashimoto, K. Shudo, T. Okamoto, M. Nagao, Y. Takahashi and T. Sugimura, Mutation Res., 1979, **66**, 191.
- 6 M.J.J. Holt and A.C. Norris, J. Chem. Educ., 1977, **54**, 426.
- 7 R.T. Coutts, D. Noble and D.G. Wibberley, J. Pharm. Pharmacol., 1964, **16**, 773.
- 8 E.E. Smissman, M.D. Corbett, N.A. Jenny and O. Kristiansen, J. Org. Chem., 1972, **37**, 1700.
- 9 J. Hase, K. Kobashi and K. Kumaki, Chem. Pharm. Bull., 1967, **15**, 534.
- 10 J.B-son Brendenberg, E. Honkanen and A.I. Virtanen, Acta Chem. Scand., 1962, **16**, 135.
- 11 H.R. Bravo and H.M. Niemeyer, Tetrahedron, in press.
- 12 S.V. Copaja, H.R. Bravo and H.M. Niemeyer, to be published.
- 13 L. Kutschabsky, W. Dathe and G. Schneider, Cryst. Struct. Comm., 1982, **11**, 841.
- 14 In this equation, total concentration of DIMBOA has been used. DIMBOA is a diprotic acid with pK_a 's of 6.9 and 10.9.¹⁵ Since at pH 9 the mono-anion corresponds to 99.7% of total DIMBOA, the error involved in this equation is negligible.
- 15 H.M. Niemeyer, H.R. Bravo, G.F. Peña and L.J. Corcuera, Chemistry and Biology of Hydroxamic Acids, H. Kehl, ed., S. Karger AG, Basel, 1982, p. 22.

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