

INTERACTION OF 2,4-DIHYDROXY-7-METHOXY-1,4-BENZOXAZIN-3-ONE (DIMBOA)
WITH ALCOHOLIC SOLVENTS

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Abstract- Solubilities and IR spectra of DIMBOA in alcoholic solvents showed that the carbonyl group of DIMBOA is hydrogen-bonded to the solvent. Activation parameters of DIMBOA in the same solvents suggested that the decomposition of DIMBOA occurs through an isocyanate, in analogy with the reaction in aqueous and aprotic solvents.

Extracts of Gramineae such as wheat and maize contain hydroxamic acids, such as DIMBOA, which are involved in the resistance of the plants to pests and pathogens.^{1,2} The study of the chemistry of DIMBOA has provided a basis for rationalizing its biological properties at the molecular level.³ The stability of DIMBOA has been described in aqueous^{4,5} and aprotic solvents.⁶ We herein describe the behavior of DIMBOA in alcoholic solvents.

Solubilities of DIMBOA were determined by adding FeCl_3 reagent to the supernatant of saturated solutions of DIMBOA and measuring the absorbance at 590 nm of the blue complex formed. Rates of decomposition of DIMBOA were followed by taking aliquots of the reaction mixture after different time intervals and analyzing them with FeCl_3 reagent.

Solubilities of DIMBOA in different alcohols generated a linear solvation energy relationship (Fig. 1) using acceptor number (AN) as solvent parameter, a measure of the ability of the solvent to accept an electron pair.^{7,8} Additionally, a 2-parameter correlation using AN and DN (donor number), a measure of the ability of the solvent to donate an electron pair,^{7,8} produced a ratio of coefficients for AN and DN equal to 25, further supporting that electron pair accepting properties of the solvent are of overwhelming importance in its interaction with DIMBOA.⁹

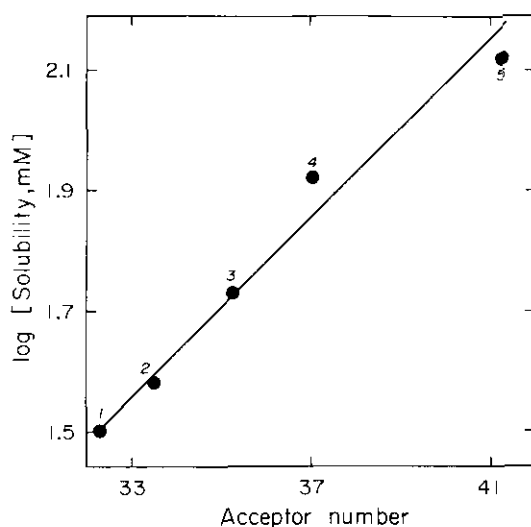


Fig. 1. Effect of the acceptor number of alcoholic solvent on the solubility of DIMBOA at 284 K. Solvents employed were: methanol (1), ethanol (2), 1-propanol (3), 2-propanol (4) and 1-butanol (5). Correlation coefficient = 0.986.

These results point to the interaction of electrophilic sites in the solvent with nucleophilic sites in DIMBOA. The former can be assumed to be the hydroxyl proton in the solvent; the latter may be identified with the carbonyl group of DIMBOA. Confirmation of this proposition was obtained from the effect of solvent on the carbonyl stretching frequency of DIMBOA. Table 1 shows that as AN increased, the carbonyl band broadened and shifted towards the region of increased single bond character, indicating hydrogen bonding of the carbonyl group to the solvent.

Table 1. Stretching frequencies and band widths of the carbonyl group in DIMBOA dissolved in alcohols

Solvent	$\nu_{C=O}(\text{cm}^{-1})$	$\Delta\nu(\text{cm}^{-1})$	AN ^a
Methanol	1672	very broad	41.3
Ethanol	1684	57	37.1
1-Propanol	1689	48	35.3
2-Propanol	1687	48	33.5
1-Butanol	1687	47	32.2
t-Butanol	1689	40	27.7

^a see note 8.

The kinetics of decomposition were first order with respect to DIMBOA. Free energies of activation produced a linear solvation energy relationship with AN (Fig. 2). In addition, an isokinetic relationship (correlation coefficient = 0.998) was generated with a value of β (363 K) falling within the range expected for solvent effects on reaction rates.¹⁰

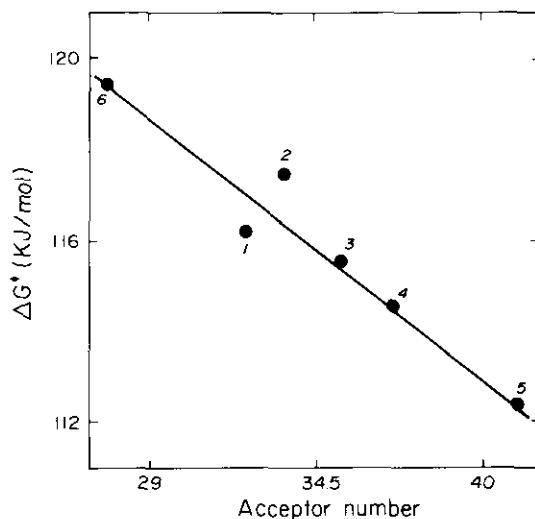
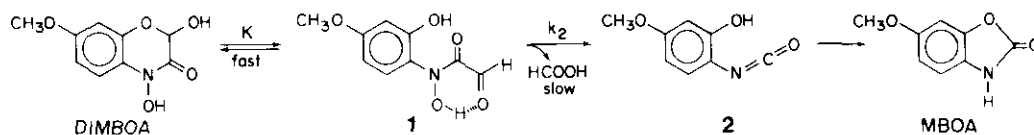


Fig. 2. Effect of the acceptor number of the alcoholic solvent on the free energy of activation of DIMBOA at 326 K. Solvents employed were the same as in Fig. 1 and t-butanol (6). Correlation coefficient = -0.980.

The main products from the reaction were 6-methoxybenzoxazolin-2-one (MBOA) and formic acid. The following mechanism incorporates the features described:



The observed rate constant is the product of the equilibrium constant for hemiacetal opening (K) times the rate constant for isocyanate formation (k_2). Intermediate 1 has a carbonyl group engaged in intramolecular hydrogen bonding and a carbonyl group relatively free to interact with the solvent. Thus 1 does not differ substantially from DIMBOA in capability of interaction with solvent

in the manner previously described. Hence, electron pair accepting properties of the solvent are not expected to show a substantial influence on the value of K . On the other hand, during formation of the transition state leading to isocyanate 2, the intramolecular hydrogen bond in 1 must be broken to allow attack by the hydroxamic hydroxyl group on the aldehydic carbon. This process is expected to be facilitated by accepting solvents which not only compete with the hydroxamic hydroxyl group for interaction with the carbonyl group but also polarize it increasing its receptivity towards nucleophilic attack. This is borne out by the free solvation energy relationship of Fig. 2.

A mechanism similar to that presented has been postulated for the decomposition of DIMBOA in aqueous⁴ and aprotic^{6,11} solvents.

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