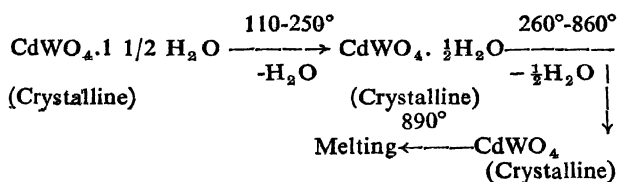


Thus, the thermal changes in cadmium tungstate may be expressed as follows :



### Acknowledgement

The authors are thankful to the Physical Research Wing and Catalyst Section, P & D Division, F. C. I., Sindri for their help in taking the TG analysis and X-ray diffraction patterns of cadmium tungstate.

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### Role of Organic Heterocyclic Compounds as Corrosion Inhibitors for Copper and Brass (63/37) in Ammonium Chloride Solution

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**B**RASS sheets (26 S. W. G.) of the composition Cu-63.3% and Zn-36.7% and copper sheets (26 S. W. G.) of the composition Cu-99.6% and Fe and other metals 0.4% were used.

The specimens were cleaned and polished as usual<sup>1</sup>. For the immersion of the specimens, 250 ml solution of the ammonium chloride (1N) was taken. The influence of current density on the metals was also studied according to the Evans' diagram as described earlier<sup>2</sup>.

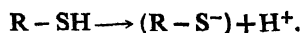
### Results and Discussion

The inhibitive power of BTA, BMA, IDA, 2-MBT, 2-MBMA and 2-MBO) increases with increase in concentration of the inhibitor (Table 1). They are effective at a concentration of 200 ppm.

TABLE 1—LOSS IN WEIGHT DATA FOR COPPER AND BRASS (63/37) IN 1N AMMONIUM CHLORIDE SOLUTION WITH VARIOUS AZOLES AS INHIBITORS.

Inhibitor	Concentration of inhibitor ppm	Copper		Brass (63/37)	
		Loss mg/dm <sup>2</sup>	Inhibition %	Loss mg/dm <sup>2</sup>	Inhibition %
2-mercaptobenzothiazole (2-MBT)	00	174.0	—	76.4	—
	10	133.0	23	62.2	19
	20	128.0	26	52.2	32
	40	126.0	27	33.2	50
	100	88.0	49	21.4	72
2-mercaptobenzimidazole (2-MBMA)	200	43.6	75	12.5	84
	10	167.0	5	15.3	80
	20	85.3	51	12.3	84
	40	63.3	64	2.3	96
	100	42.2	76	1.9	97
Benzotriazole (BTA)	200	30.5	83	1.9	97
	10	133.0	24	5.5	93
	20	111.0	36	2.2	97
	40	59.4	66	1.7	98
	100	34.2	80	0.8	99
Benzimidazole (BMA)	200	0.3	~100	0.3	100
	10	162.0	9	73.9	3
	20	134.0	23	69.5	9
	40	104.0	41	43.5	43
	100	18.6	90	21.7	82
Indole (IDA)	200	9.7	94	6.1	92
	10	133.0	24	69.4	9
	20	128.0	27	65.3	14
	40	107.0	39	62.6	28
	100	100.0	43	36.2	50
2-mercaptobenzoxazole (2-MBO)	200	10.5	94	12.8	87
	10	2.0	99	2.0	99
	20	1.0	100	1.0	100
	40	1.0	100	1.0	100
	100	1.0	100	1.0	100
200	1.0	100	1.0	100	

The mercapto heterocyclic compounds are weak thio-acids ionizing as



The ionic species form insoluble complex salt  $[\text{Cu}(\text{R-S}^-)_2]$  with metal (copper) ion. This complex acts as the protective coating on the metal surface. The possible structure of the insoluble film for copper surface is coherent. The inhibition afforded by BTA and BMA is due to complex film formation. In case of indole, it is adsorbed on the metal surface by electrostatic forces. There is little possibility of complex formation.

From the polarisation data, (not given for the sake of brevity), the rise in cathodic potential on the addition of inhibitors may be due to the formation of an insoluble film on cathode. The cathode potential will vary as determined by Tafel's rule.

**Acknowledgement**

The authors' thanks are due to Gujarat University and C. S. I. R. for granting a senior scholarship to one of them (S. N. P.).

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**Decarboxylation of Oxamic Acid in Resorcinol and Catechol**

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CLARK<sup>1</sup> has made extensive studies on the decarboxylation of oxamic acid in several non-aqueous solvents. Oxamic acid decarboxylates in resorcinol and catechol in a manner similar to that of oxanilic acid<sup>2</sup>. No kinetic data have been reported for the decarboxylation of oxamic acid in these solvents.

**Experimental**

**Reagents:** Oxamic acid used was an analytical reagent grade, m.p., 212°. Resorcinol and catechol were BDH analytical reagents. No further purification of these chemicals was done.

**Apparatus and technique:** The kinetic experiments were conducted in a constant temperature oil-bath ( $\pm 0.05^\circ$ ) by measuring the volume of CO<sub>2</sub> gas evolved at constant pressure. The apparatus and technique are the same as described in our previous articles<sup>3,4</sup>. 0.1586 g of oxamic acid was taken in about 50g of resorcinol and 50 g. of catechol separately and allowed to decompose in a constant temperature oil-bath. The CO<sub>2</sub> gas was collected at room temperature in a measuring burette filled with water which had been previously saturated with carbon dioxide.

**Results and Discussion**

The decarboxylation of oxamic acid was studied at seven different temperatures. The log (V<sub>∞</sub> - V<sub>t</sub>) vs t, plot resulted in a straight line in all the experiments indicating that the reaction is of first order, where V<sub>∞</sub> is the maximum volume of CO<sub>2</sub> after complete decomposition and V<sub>t</sub> is the volume at time t. The rate constants were calculated from the slopes of the graphs and are tabulated in Table 1. The Arrhenius parameters of Eyring equation based upon the data of Table 1 are shown in Table 2.

TABLE 1—FIRST-ORDER RATE CONSTANTS FOR THE DECARBOXYLATION OF OXAMIC ACID IN RESORCINOL AND CATECHOL.

Temp °C	No. of data pairs	Av. k <sub>1</sub> × 10 <sup>4</sup> sec <sup>-1</sup> Resorcinol	Av. k <sub>1</sub> × 10 <sup>4</sup> sec <sup>-1</sup> Catechol
140	3	2.57 ± 0.01	1.82 ± 0.02
145	4	4.57 ± 0.01	3.31 ± 0.03
150	5	8.71 ± 0.02	6.03 ± 0.01
155	4	15.49 ± 0.01	9.57 ± 0.03
160	3	26.31 ± 0.02	13.38 ± 0.04
165	2	42.66 ± 0.04	28.84 ± 0.05
170	2	75.87 ± 0.05	48.98 ± 0.05

TABLE 2—COMPARISON OF THERMODYNAMIC PARAMETERS.

Solvents	Resorcinol	Catechol
E <sub>a</sub> kcal mole <sup>-1</sup>	38.95 ± 0.2	35.97 ± 0.2
log A (sec <sup>-1</sup> )	17.05 ± 0.01	15.27 ± 0.02
ΔH <sup>‡</sup> (kcal mole <sup>-1</sup> )	38.14 ± 0.3	35.14 ± 0.4
ΔS <sup>‡</sup> (cal mole <sup>-1</sup> deg <sup>-1</sup> )	+13.30 ± 0.3	+10.12 ± 0.3
ΔF <sup>‡</sup> (kcal mole <sup>-1</sup> )	31.06 ± 0.2	31.62 ± 0.5
k <sub>1</sub> × 10 <sup>4</sup> (sec <sup>-1</sup> ) at 160°	26.31	13.38

The decarboxylation of oxamic acid is kinetically first order in both the solvents at the run temperatures of this investigation and the reaction is faster in resorcinol than in catechol, like other carboxylic acids<sup>2-5</sup>. No such abnormal behaviour has been observed as shown by oxanilic acid<sup>2</sup> in these solvents. It has been reported earlier that the single hydroxyl group of resorcinol associates with the carbonyl group of the acid while the other hydroxyl group remains isolated. In catechol the acid associates with the two adjacent, hydroxyl groups of catechol. Hence the bulkier intermediate complex in catechol than in

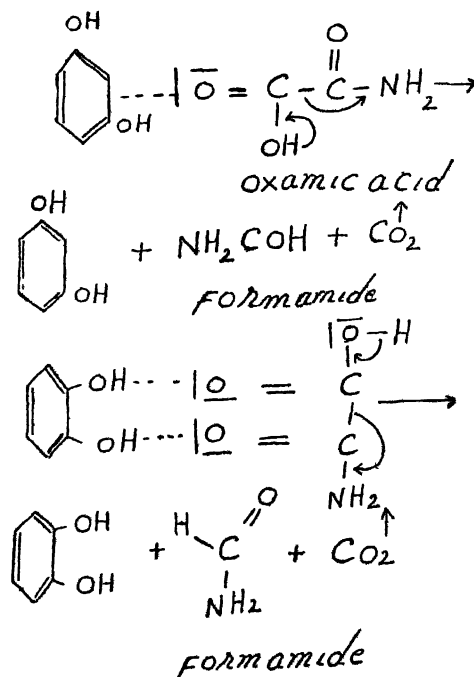


FIG. 1