The Effect of Some β-Diketo Compounds on the Corrosion of Zinc in Hydrochloric Acid Solution

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The dissolution of zinc metal in aqueous hydrochloric acid solution (2N) was followed periodically by measuring the amount of evolved hydrogen. The inhibition efficiencies of these β-diketo compounds were evaluated as the percentage reduction in reaction rate. The results obtained were also compared with those employing thermometric method.

It is shown that β-diketo compounds act as corrosion inhibitors. The results obtained indicate that the adsorption of β-diketo compounds occurs over the zinc surface through their carbonyl groups and N-atom in two step adsorption processes.

THE dissolution of many metals in acidic solutions is usually accompanied by hydrogen evolution. The dissolution rate of zinc has been studied[1] by measuring the volume of the hydrogen evolved in presence and in absence of aromatic amines. Diphenylethylarsine was used as corrosion inhibitor[2] for zinc in perchloric acid solution and it was found that the corrosion decreased by 85%. The effect of salts of nitroaromatic acids on the corrosion behaviour of zinc in neutral aqueous medium was studied[3]. The use of n-decylamine as corrosion inhibitor was proved[4]. Recently a simple and rapid method has been developed[5] based on the thermometric corrosion test of Mylius[6]. This method has been successfully used[7-13] for comparing the inhibition efficiency of different organic additives in reducing the dissolution of aluminium and zinc in hydrochloric acid. The object of the present investigation is to throw some light on the use of the β-diketo compounds as corrosion inhibitors for zinc in acid solution.

Experimental

Inhibitor (I), sodio-derivative of 6-ethoxy carbonyl-5H-1-pyridine-5,7-6H-dione, was prepared by Claisen condensation of pyridine-2,3-dicarboxylic acid ester with ethylacetate in presence of sodium ethoxide[14].

Inhibitor (II), 6-acetyl-5H-1-pyridine-5,7 (6H)-dione, was prepared by Claisen condensation of pyridine-2,3-dicarboxylic acid ester with acetone in presence of sodium ethoxide[15].

Inhibitor (III), sodio-derivative of 2-ethoxycarbonyl-5-nitro-1,3-indandione, was prepared by Claisen condensation of 3-nitrophthalic acid ester with ethylacetate in presence of sodium ethoxide[16].

Inhibitor (IV), sodio-derivative of 2-ethoxy carbonyl-1,3-indandione, was prepared by Claisen condensation of diethyl phthalate with ethylacetate in presence of sodium ethoxide[17].

Inhibitor (V), 2-(o-hydroxy-benzylidene)-1,3-indandione, was prepared by condensation of 1,3-indandione with o-hydroxybenzaldehyde[18].

2N HCl solution was used in all experiments. Zn test pieces measuring $1 \times 10 \times 100$ mm were used for thermometric, while $1 \times 20 \times 20$ mm test pieces were used for hydrogen evolation method. These were degreased and etched[11].

In the hydrogen evolution method, the reaction vessel and the procedure for determining the dissolution of zinc in the corroding media were the same as described previously[19].

The efficiency of a given inhibitor can be evaluated as the percentage reduction in reaction rate (RR), % Inhibitor efficiency

$$= \frac{\text{RR uninhibited} - \text{RR inhibited}}{\text{RR uninhibited}} \times 100$$

The procedure for the determination of metal dissolution rate by the thermometric method has been described previously[5].

The reaction number, RN, is defined as

$$RN = (T_{max} - T_i)/t$$

where T_{max} and T_i are the maximum and initial temperatures, respectively, and t is the time required to reach the maximum temperature, in minutes.

The percentage reduction in reaction number is given as[20]

$$\frac{\text{RN uninhibited} - \text{RN inhibited}}{\text{RN uninhibited}} \times 100$$

Results and Discussion

Zinc dissolves rapidly in $2N$ HCl. The maximum temperature is 38.2°, and is attained within 14 min, correspoding to a reaction number, RN, of 0.943° min^{-1} (curve a, Fig. 1). When to the HCl solution
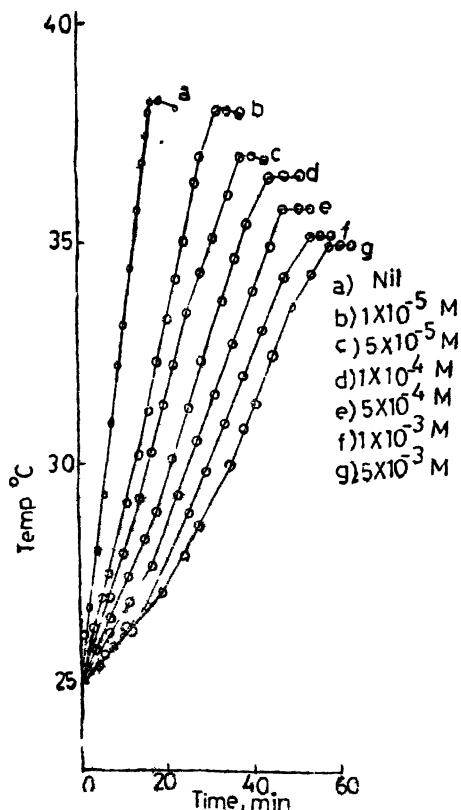
in absence and in presence of different concentrations of inhibitor I. It is evident that the weight loss-time curves are typical kinetic ones with a slope
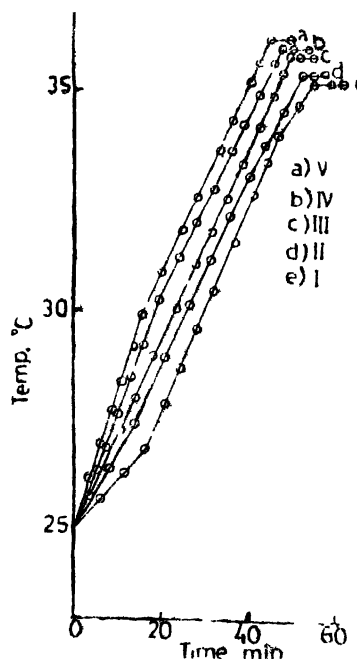

Fig. 1. Temp.-time curves obtaind in absence and in presence of varying concentration of inhibitor (I).

Fig. 2. Temp.-time curves for all inhibitors used at concentration $1 \times 10^{-3} M$.

increasing amounts of β-diketo compounds are added, the thermometric curves are influenced. The effect depends on the concentration of the additive used, as well as on the nature of the aggressive solution. The curves of Fig. 1 represent the behaviour observed in the presence of additions of inhibitor I. The curves for additive containing systems fall below that of the free acid. This indicates that the additive behaves as inhibitors over the concentration range studied. Curves having the same character are obtained with the other tested materials. For comparison, selective temperature-time and weight loss-time curves for the five β-diketo compounds are given in Figs. 2 and 6.

Fig. 3 represents the reaction number RN of the system to the logarithm of concentration of the inhibitor I. Fig. 4 relates to the logarithm of the time delay, $\triangle t$, with log C for the various systems. Table 1 shows the effect of concentration of the various inhibitors on the percentage reduction in reaction number, RN.

Fig. 5 represents the weight loss-time curves of the system involving zinc in $2N$ HCl was observed
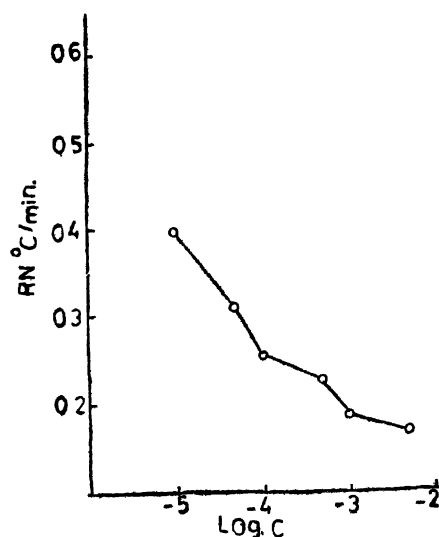

Fig. 3. Reduction in RN vs log C for inhibitor (I).

TABLE 1—EFFICIENCY OF CORROSION INHIBITION AS DETERMINED BY PERCENTAGE REDUCTION IN RN

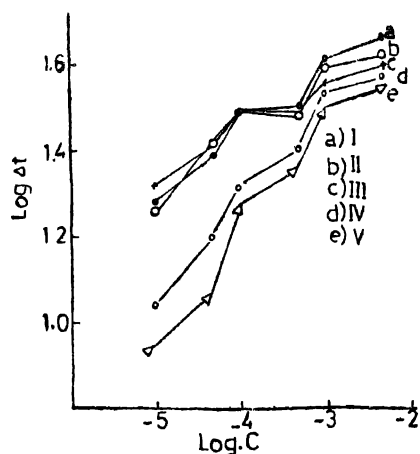| Concn. of the inhibitor	% Reduction in RN				
	I	II	III	IV	V
1×10^{-5}	58 22	56.96	59.13	45.71	43.80
5×10^{-5}	67.34	67.13	68.19	57.58	54.29
1×10^{-4}	72 85	71.05	70.00	65.11	64.37
5×10^{-4}	76.14	73 49	73.17	69.57	68.50
1×10^{-3}	80.38	79.22	77.09	75.72	73.59
5×10^{-3}	82.29	80.70	79.22	77.94	76.25

Fig. 4. Log of time delay Δt vs log concentration of inhibitor relationship for the various systems.

TABLE 2—COMPARISON BETWEEN EFFICIENCY OF CORROSION AS DETERMINED BY THERMOMETRIC AND HYDROGEN EVOLUTION TECHNIQUES

Inhibitor added	Rate of dissolution* mg cm⁻² min⁻¹	% Reduction in RR	% Reduction in RN
Nil	15.20	–	–
V	6.00	62.50	64.37
IV	4.50	70.39	65.11
III	3.30	78.29	70.00
II	2.30	84.87	71.05
I	1.50	90.13	72.85

* At 10 min from the beginning of dissolution.
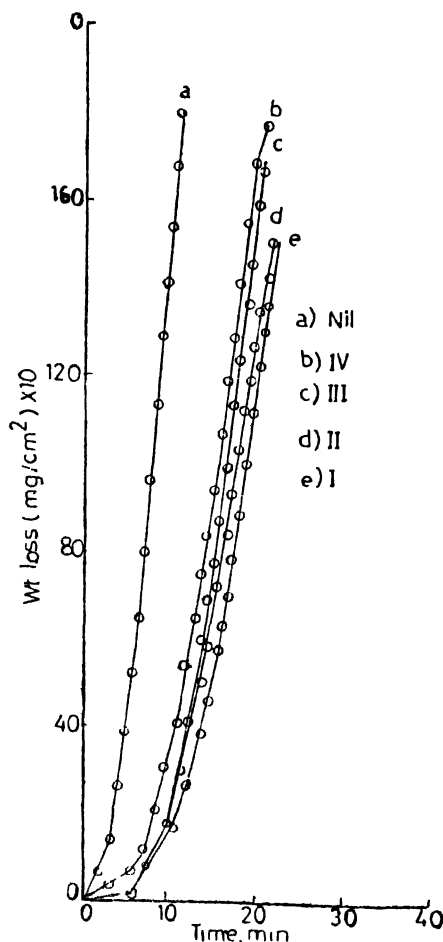
Fig. 6. Wt. loss-time curves for all inhibitor used at concentration $1 \times 10^{-4}M$.
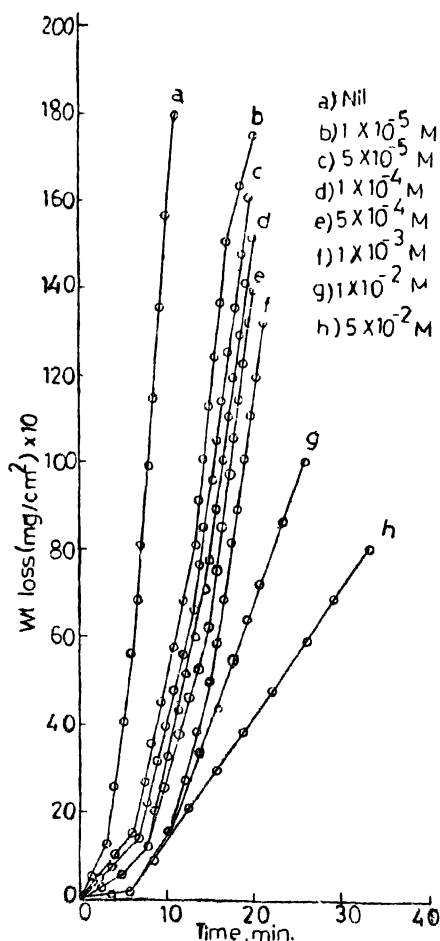

Fig. 5. Wt. loss-time curves for inhibitor (I).

representing the reaction rate at any time. Included in Table 2 are the percentage reduction in RR for all the systems at concentration of $1 \times 10^{-4}M$.

The corrosion rates were also determined at 20, 30, 35 and 40° in the presence of $1 \times 10^{-4}M$

β-diketo compounds used. These results are recorded in Table 3. Activation energy for the corrosion process of each inhibitor was evaluated by plotting log corrosion rate against reciprocal of T, in degree absolute (Fig. 7). The free energy of activation was calculated using Gibb's equation and the entropy of activation using transition state theory[21]. Energy, entropy and Gibb's free energy of activation for different β-diketo inhibitors are recorded in Fig. 7.
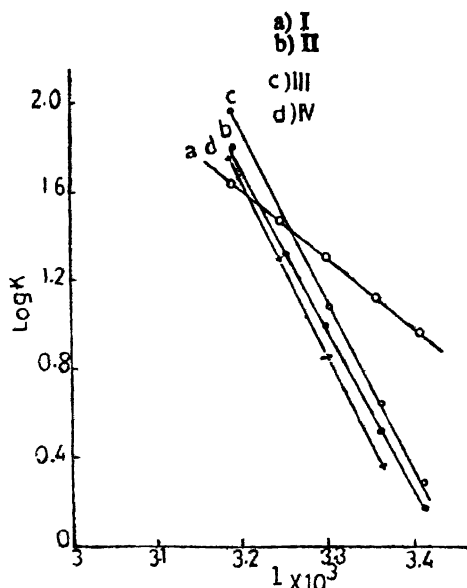
Fig. 7. $\log K - \frac{1}{T}$ curves for Zn dissolution in presence of various inhibitors.

	Ea, k cal	S*, e.u	G*, j × 10⁻¹
I	20.3	11.8	81.136
II	18.4	6.8	74.946
III	14.7	− 5.7	63.639
IV	7.4	−28.6	39.485

Table 3—Corrosion Rates in mg cm⁻² min⁻¹ for Zinc Dissolution at Different Temperatures in the Presence of 1 × 10⁻⁴ M β-Diketo Inhibitors

Inhibitor	temp., deg⁻¹				
	20	25	30	35	40
IV	−	4.50	6.92	19.05	57.54
III	1.91	3.30	12.02	30.20	91.20
II	1.15	2.30	10.00	20.89	63 10
I	9.12	1.50	19.95	28.84	43.65

The thermometric curves representing the dissolution of zinc in HCl, Fig. 1, differ from those for aluminium[11] in that the incubation and the induction periods are absent. The temperature of the system rises almost linearly from the moment the metal is allowed to react with the aggressive electrolyte. The air-formed oxide on the Zn metal, in contrast to that on Al, does not offer any resistance to the acid attack. The curves obtained in the presence of increasing concentrations of the inhibitors indicates that the additive is strongly adsorbed on the anodic sites of the metal. The same characeristtic can be noticed in hydrogen evolution (Fig. 5) method.

Fig. 3 representing the reaction number -log C curves consist of an initial descending portion along which RN decreases with increasing β-diketo inhibitor concentration up to a certain limit. Above this limit the rate of decrease in RN values becomes smaller as revealed from the smaller values of the slope. However, as the concentration of the additive increases further, the values of RN decrease linearly with concentration and then become almost constant. This behaviour is explainable on the

basis of two-step adsorption process. The plots of log Δt vs log C confirms this explanation. The curves consist each of an initial linear portion which passes to a region of constancy. There is again a second rise in log Δt before the values attain constancy. The first constancy is an indication of the completion of a monolayer of the adsorbate. The second region of constancy indicates the formation of the second layer.

The data in Table 1 indicate that the efficiency of corrosion inhibition as calculated from the reduction in RN varies with both the type and the concentration of the β-diketo inhibitor used.

The inhibition efficiency, expressed as the percentage reduction in RR or RN, of $1 \times 10^{-4} M$ inhibitor solutions decreases in the order I>II>III>IV>V (Table 2). This indicates the validity of the results obtained by the two methods used.

In all cases, the increase in the inhibitor concentration was accompanied by a decrease in hydrogen evolution (Fig. 5), and hence an increase in the percentage reduction in RR. This was valid for all the inhibitors examined. The order of inhibitive action of the inhibitors remains the same at all the concentrations used.

The increase of percentage inhibition with increase of inhibitor concentration suggests that inhibition is due to the adsorption of these inhibitors on the Zn surface.

The results obtained in Table 3 indicate that corrosion rate increases with increasing temperature and obeys the Arrhenius law[22] (Fig. 7) in the range of temperature used.

The corrosion process is controlled by the surface reaction, since the energy of activation for the corrosion process is above 5 k cal (Fig. 7).

It is clear that carbonyl group and nitrogen atom are the centres involved in the adsorption of the inhibitors over the metallic surface[23]. The inhibition efficiency of the studied β-diketo inhibitors depends on the number of centres of adsorption and on the charge density of the inhibitors. Inhibitor I has four centres of adsorption (three C=O and one N), inhibitor II has the same centres of adsorption but its basicity is lesser than inhibitor I due to the presence of α-hydrogen atom with respect to 1,3-dione which forms hydrogen bond, inhibitor III has four centres of adsorption (three C=O and one N) but its basicity is lesser than the above two inhibitors due to the electron attracting character of the nitro group, inhibitor IV has only three centres of adsorption (three C=O), and inhibitor V has only two centres of adsorption (two C=O).

This explanation is in agreement with the results obtained in Table 2 which give the efficiency of inhibition of the β-diketo inhibitors studiel, it increases with increasing the charge density on these inhibitors.

References

1. L. Z. VORKAPIC, A. R. DESPIC and D. M. DRAZIC, *Glas. Hem. Drus. Beograd*, 1977, **42**, 757.
2. H. B RUDRESH and S. M. MAYANNA, *Surf. Technol.*, 1911, **6**, 139.
3. A. I. TRUFANAVA and V. U. ERMOSHINA, *Sint. Anal. Strukt. Org. Soedin*, 1976, **7**, 77.
4. H. B. RUDRESH and S. M. MAYANNA, *Br. Corros. J.*, 1977, **12**, 54.
5. K. AZIZ and A. M. SHAMS EL DIN, *Corrosion Sci.*, 1965, **5**, 489.
6. F. MYLIUS, *Z. Metall.*, 1922, **14**, 233.
7. I. M. ISSA, A. A. EL-SAMAHY and Y. M. TEMERK, *U.A.R. J. Chem.*, 1970, **13**, 121.
8. J. M. ABD EL KADER and A. M. SHAMS EL DIN, *Corrosion Sci.*, 1970, **10**, 551.
9. R. M. SALEH and A. M. SHAMS EL DIN, *Corrosion Sci.*, 1972, **12**, 689.
10. A. Z. EL HOSARY, R. M. SALEH and A. M. SHAMS EL DIN, *Corrosion Sci.*, 1972, **12**, 897.
11. I. M. ISSA, M. H. MOUSSA and A. A. GANDOUR, *Corrosion Sci.*, 1973, **13**, 791.
12. G. M. SINGAB, M.Sc. Thesis, Mansoura University, Egypt, 1975.
13. M. N. H. MOUSSA, R. I. M. TAHA, M. M. A. GOUDA and G. M. SINGAB, *Corrosion Sci.*, 1976, **16**, 379.
14. K. BITTNER, *Ber.*, 1902, **35**, 1411.
15. W. MOSHER, T. EL-ZINMAITY and D. LIPP, *J. Org. Chem.*, 1971, **36**, 3890.
16. S. MORSI, M.Sc. Thesis, Mansoura University, Egypt, 1975.
17. W. WISLICENUS, *Ana. Chem.*, 1888, **246**, 349.
18. S. KOSTANECKI and L. LACZKOWSKI, *Ber.*, 1897, **30**, 3138.
19. S. M. HASSAN, Y. A. ELAWADY, A. I. AHMED and A. O. BAGHLAF, *Corrosion Sci.*, 1979, **19**, 951.
20. B. SANYAL and K. SRIVASTAVA, *Corrosion Sci.*, 1974, **14**, 635.
21. K. J. LAIDLER, "Reaction Kinetics", Pergamon Press, London, 1963, Vol. 1.
22. V. A. KHITROV, Izv. VOROUEZHSK, *Gos. Ped. Inst.*, 1960, **29**, 5.
23. A. S. FOUDA, Ph.D. Thesis, Mansoura University, Egypt, 1979.