33. A Kinetic Study of Organic Inhibitors of the Reaction between Magnesium and Acids.

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This paper extends to the system magnesium–acid, previous observations by other authors of the inhibition of metal–acid reactions by organic substances and presents simplified methods for studying the kinetics of such inhibitions.

The dissolution of magnesium by acids has been found to be inhibited by organic amines. The dissolution reaction is of zero order in the presence of excess of acid, with an energy of activation of about 4000 cals./g.-mol. which is not greatly altered by the presence of inhibitor. Various reaction-rate constants have been determined. The relation between inhibitor concentration and degree of inhibition is found to be that expected for an adsorption process. The effectiveness of the inhibitor depends on steric factors—the shape and size of its molecule regarded as adsorbed on the metal surface at an active point.

It has long been known that certain organic compounds can inhibit the attack on metallic surfaces by acids and other corroding agents. Investigations have been made into the inhibiting properties of a variety of substances, ranging from simple aliphatic amines to large colloidal molecules, chiefly with a view to practical application. From this body of data the following widely-accepted generalisations have been drawn. First, organic inhibitors act only in so far as they are adsorbed on the metal surface, since it is found that the activity of the inhibitor in depressing the reaction rate when expressed as a function of its concentration is a typical adsorption isotherm (Mann, Lauer, and Hultin, *Ind. Eng. Chem.*, 1936, **28**, 159, 1046). The presence of an adsorbed film of organic base has actually been demonstrated in one case (Rhodes and Kuhn, *ibid.*, 1929, **21**, 1066). Further, compounds having inhibitor properties are either colloidal electrolytes or molecules which form co-ordination complexes (*e.g.*, amines, ethers, thio-compounds, unsaturated hydrocarbons). Secondly, closely related compounds, though held to the metallic surface by the same active group, have widely different inhibiting powers. These differences may be explained by steric factors—an inhibitor molecule blankets an area of the metallic surface dependent on its shape and size.

Very little work has been done to elucidate the exact mechanism of these inhibitions; indeed, there is still no general agreement on the mechanism of the primary reaction between metals and acids which, like many heterogeneous reactions, has complicated kinetics unless simplifying conditions are chosen. It is only under similar simplified conditions that we can hope to obtain an insight into the mechanism of the inhibited reaction. A simple molecule as the inhibitor and a highly electropositive metal dissolving in a dilute strong acid provide the simplest conditions possible and help the theoretical analysis of the problem even though efficient "inhibition" in the practical sense is not achieved.

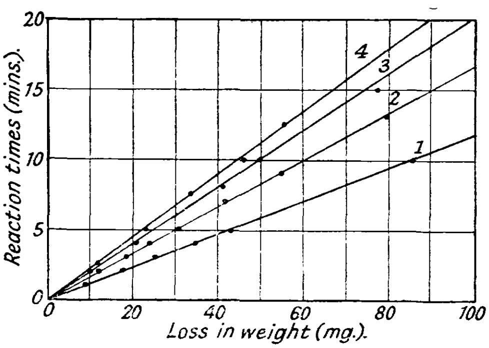
Experimental.

Hollow cylinders of magnesium, 2·0 cm. long and 0·9 cm. in diameter, were turned from rods of the pure metal. The preparation of the surface was found to be the most important single factor affecting reproducibility of the rate constants. Chemically etched surfaces gave erratic results and only mechanically polished surfaces were satisfactory. The cylinder was cleaned from oxide and grease and then polished with superfine emery paper. Particles of abrasive and metal were swabbed off with cotton-wool moistened with alcohol. Re-preparation of the surface was necessary after each run, especially when strongly inhibiting solutions were used. Reproducibility of ±2% was obtained with the same cylinder when prepared in this way. After being weighed, a prepared cylinder was secured to an ebonite rod passing through it by ebonite nuts and rubber washers at each end, and the whole was screwed together tightly so that only the external cylindrical surface was exposed. The rod was held vertically in a chuck which could be rotated at high speed through gearing from a constant-speed motor and which could be raised and lowered while rotating. The corrosive solution (500 c.c.) was placed in a bolt-head flask immersed in a thermostat kept at the desired temperature to within ±0·05°, and allowed to come to bath temperature. The motor was then started, and after reaching constant speed the rod and cylinder were lowered into the solution. At the end of the reaction period the rod was raised and a stream of water played on the cylinder as it slowed down. The detached cylinder was then washed thoroughly with distilled water, dried in a stream of warm air, and weighed. The raising and lowering of the cylinder occupied less than a second each in the usual total time of four minutes.

According to various workers (King and Cathcart, *J. Amer. Chem. Soc.*, 1937, **59**, 63; King and Schack, *ibid.*, 1935, **57**, 1212; Durdin and Markovitch, *J. Gen. Chem. Russia*, 1936, **6**, 236; Kilpatrick and Rushton, *J. Physical Chem.*, 1930, **34**, 2180), the reaction in the presence of a large excess of acid is of zero order. To check this under our conditions the same cylinder, freshly prepared each time, was rotated for various periods in an acid solution. Results obtained in a sodium acetate–hydrochloric acid mixture (pH = 1·09; see Walpole, *Biochem. J.*, 1914, **8**, 637) in 0·1N-acetic acid and in 0·1N-sulphuric acid are shown graphically in Fig. 1. In each case the loss in weight is proportional to reaction time, and it is therefore legitimate to take the loss during any convenient time as a measure of the rate constant. In all further experiments a period of 4 minutes was used, long enough to give an accurately weighable loss of metal, but not enough to change the diameter of the cylinder appreciably, or the amount of acid present.

FIG. 1.

Loss of weight of magnesium cylinders in acid solution at 25°.



1. 2 × 0·9 *cm.*, 2150 *r.p.m. in* 500 *c.c.* 0·1N-H_2SO_4.
2. 2 × 0·9 *cm.*, 1300 *r.p.m. in* 500 *c.c.* 0·1N-H_2SO_4.
3. 2 × 0·9 *cm.*, 1300 *r.p.m. in* 500 *c.c. acetate*–HCl *mixture* (pH = 1·09).
4. 3 × 0·9 *cm.*, 2150 *r.p.m. in* 400 *c.c.* 0·1N-*acetic acid.*

In order to extend the above procedure to the measurements of inhibiting power, a given cylinder, after duplicate runs in fresh portions of the acid solution, was again run twice in portions of acid to which the desired concentration of inhibitor had been added. The ratio

$$\frac{\text{Average loss in weight in solution with inhibitor}}{\text{Average loss of weight in pure acid solution}} \times 100$$

was termed the "relative corrosion," and was independent of actual loss of weight, which varied slightly from cylinder to cylinder since the dimensions were not all the same. The simple aliphatic amines are not very efficient inhibitors of the metal–acid reaction, and with magnesium and strong acids it was found that the main effect of adding the base was neutralisation. The reactions were therefore carried out in the sodium acetate–hydrochloric acid mixture referred to above. Large additions of amine could be made to it without sensible alteration of its pH of 1·09. Heterocyclic nitrogen compounds were much better inhibitors. Typical results are given in Table I, piperidine being the inhibitor.

TABLE I.

Acid : NaOAc–HCl mixture.
Time : 4 minutes.

Inhibitor : piperidine.
Temperature : 25°.

Concn. of inhibitor m.-mols./l.	Loss of wt. in acid (g. × 10^{-4}).			Loss of wt. in acid plus inhibitor (g. × 10^{-4}).			Relative corrosion.
5	216	210	Mean 213	185	181	Mean 183	88·8
10	199	197	198	162	161	161·5	82·0
15	196	201	198·5	154	148	151	76·0
20	198	202	200	140	144	142	71·0
30	202	204	203	129	125	127	62·5
40	198	205	201·5	107	112	109·5	54·1
60	197	202	199·5	90	93	91·5	48·9
80	200	204	202	85	81	83	41·2
100	204	199	202·5	70	75	72·5	36·0

RESULTS AND DISCUSSION.

Calculation of Rate Constants.—It has been stated (King and Schack, *loc. cit.*) that the rate of reaction is directly proportional to the velocity of the surface through the solution at speeds above 1000 cm./minute. Speeds used in this study were 1300 r.p.m. and 2150 r.p.m., giving for cylinders 0·9 cm. in diameter a linear velocity through the solution of 3675 and 6080 cm./minute, respectively. The ratio obtained by comparing the slopes of curves 1 and 2 in Fig. 1 shows that in the present case the rates are roughly, but not exactly, proportional to these velocities (ratio of speeds = 1·65; ratio of reaction velocities = 1·43). Kilpatrick and Rushton's relationship (*loc. cit.*), *i.e.*, reaction velocity proportional to (speed of rotation)$^{0\cdot29}$, gives a calculated ratio of reaction velocities of 1·157, agreeing even less well. It was decided to use King and Schack's relationship in comparing the data of the present study with those of previous workers. The special first-order formula used in both the investigations just referred to was thus adjusted for speed of rotation and a constant k was calculated from the formula

$$k = \frac{2{\cdot}303V}{At} \,.\, \log\frac{a}{(a-x)} \,.\, \frac{1000}{L}$$

where V = volume of solution, in ml.; A = area of cylinder surface, in square cm.; t = time of run, in minutes; a = dissolving capacity of solution, in any units; x = amount dissolved, in the same units; L = linear speed of cylinder surface, in cm./minute.

TABLE II.

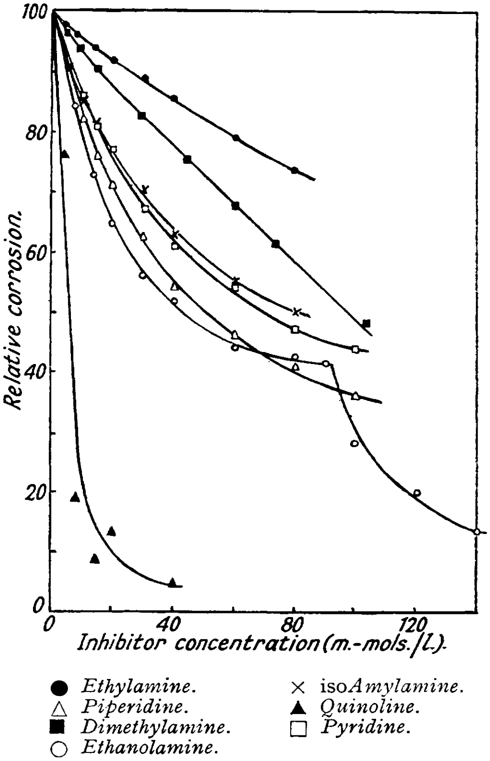
Corroding solution.		Linear speed, cm./min.	k.	Observers.*
H_2SO_4	0·05N	6080	0·205	H. and J.
,,	0·0575N	2000	0·229	K. and C.
,,	0·1N	6080	0·202	H. and J.
,,	0·1N	3675	0·242	,,
,,	0·15N	6080	0·201	,,
$CH_3{\cdot}CO_2H$	0·05N	6080	0·075	,,
,,	0·0597N	2000	0·090	K. and C.
HCl	0·05N	2000	0·248	,,
Acetate–HCl mixture (pH = 1·09)		3675	0·157	H. and J.
Pyridinium chloride (0·06M.) + pyridine (0·04M.)		2000	0·312	K. and C.
Pyridinium chloride (0·03M.) + pyridine (0·07M.)		2000	0·175	,,
Pyridinium sulphate (0·05M.) + pyridine (0·05M.)		6080	0·245	H. and J.

* K. and C. = King and Cathcart; H. and J. = present work.

This constant is then independent of volume used, concentration of acid, size of cylinder, and time of run, and reduces all results to a linear speed of 1000 cm./minutes. It has the dimensions cm./minute since the reaction is diffusion controlled. Table II gives the calculated values of k for various solutions used in the present work and also some recalculated from the work of King and Cathcart.

FIG. 2.

Relation between concentration and degree of inhibition in acetate–HCl *mixture at* 25°.



The table shows that the values obtained in the present work are of the same order as those obtained earlier and are in good agreement when direct comparison is possible, allowance being made for the fact that the constant is adjusted empirically for the difference in speed of rotation and is taken over only a short part of the reaction. The constant can be seen to vary with the acid used and is not directly related to the hydrogen-ion concentration. It is noteworthy that the pyridinium ion is an even more corrosive agent than the hydrogen ion and confirms the view that all the " acids " in the extended sense must be considered to take part in the reaction.

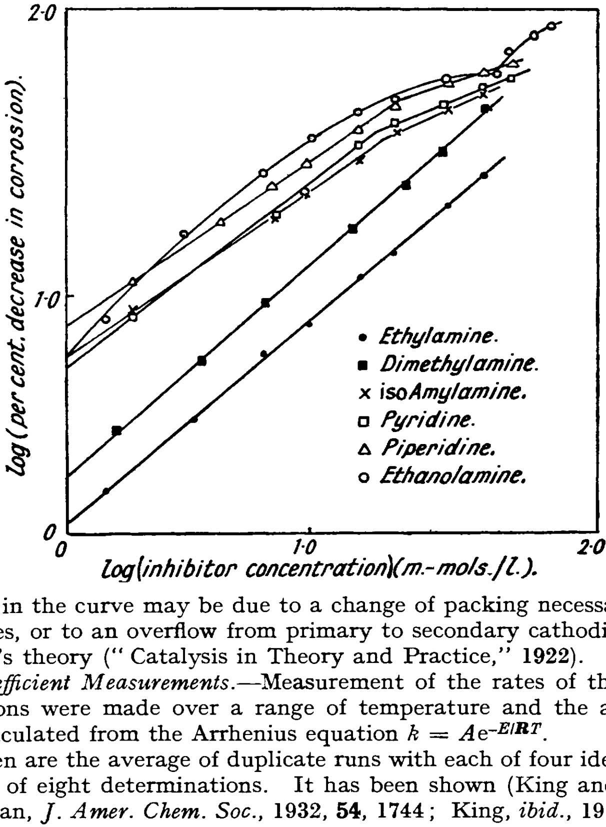
Effect of Inhibitors.—The figures for the inhibiting power of various amines in the acetate–acid mixture obtained as outlined in the experimental section are shown graphically in Fig. 2. Most of the curves are of the type to be expected if adsorption is the controlling process. The figure shows clearly the increased efficiency of inhibition due to: (*a*) increasing length of chain (compare ethylamine and *iso*amylamine), (*b*) multiplicity of chains (compare ethylamine and dimethylamine), (*c*) ring formation (compare *iso*amylamine and piperidine), (*d*) multiple rings (compare quinoline and piperidine).

These results extend to magnesium conclusions that have been reached after detailed observations of other metals (Mann, Lauer, and Hultin, *loc. cit.*) The curve for ethanolamine shows a remarkable and reproducible anomaly; this, and the greatly increased efficiency compared with the similar ethylamine, is probably due to solvation of the hydroxyl group, giving an enhanced blocking effect.

Erratic results were obtained with quinoline; an insoluble yellow complex was formed with magnesium salts giving an adherent coating so that this part of the work was discontinued.

If the results shown in Fig. 2 are plotted as log (% decrease in corrosion) against log (concentration of inhibitor), as in Fig. 3, it is clear that the relation $\log I = \log a + b \log c$ (where I = % decrease in corrosion, c = inhibitor concentration) is valid up to about 40% decrease in corrosion for all inhibitors studied. For this part the slope (b) is about 0·75. With *iso*amylamine, pyridine, and piperidine there is a second straight part of the curve with a slope of about 0·40 (cf. Mann, Lauer, and Hultin, *loc. cit.*). If we assume that the inhibiting action is controlled by adsorption from the liquid on the solid metal, the values of b are of the right order. The break in the curve may be due to a change of packing necessary to accommodate the larger molecules, or to an overflow from primary to secondary cathodic areas according to Taylor and Rideal's theory (" Catalysis in Theory and Practice," 1922).

FIG. 3.



Temperature-coefficient Measurements.—Measurement of the rates of the inhibited and the uninhibited reactions were made over a range of temperature and the apparent energies of activation were calculated from the Arrhenius equation $k = Ae^{-E/RT}$.

The results given are the average of duplicate runs with each of four identical cylinders and are thus the mean of eight determinations. It has been shown (King and Cathcart, *loc. cit.*; King and Braverman, *J. Amer. Chem. Soc.*, 1932, **54**, 1744; King, *ibid.*, 1935, **57**, 828) that the observed energy of activation for the dissolution of metals by strongly acid solutions is probably, in fact, an energy of diffusion; the values found agree with that to be expected for a diffusion energy and are extremely low for a true activation energy. The mean energy of activation found in this study (3800 cals./g.-mol.) agrees with that found by other observers.

Whatever the mechanism, it is obvious from Table III that it is not inherently altered by the presence of inhibitors. Areas of surface are apparently blocked off, but the residual reaction is the same as before.

TABLE III.

Concn. of inhibitor (m.-mols./l.).	Loss of wt. (10^{-4}g.) at :				Energy of activation (cals./mol.) :			
	15°.	25°.	35°.	45°.	25°/15°.	35°/25°.	45°/35°.	Mean.
0	158	199	245	296	3950	3790	3680	3800
20	—	154	197·5	248	—	4550	4450	4500
40	—	129·5	165	204	—	4460	4300	4380
60	—	107·5	135·5	167	—	4230	4170	4200
80	—	94	118	145	—	4160	4080	4120
100	—	84·5	105	128	—	3960	3820	3890

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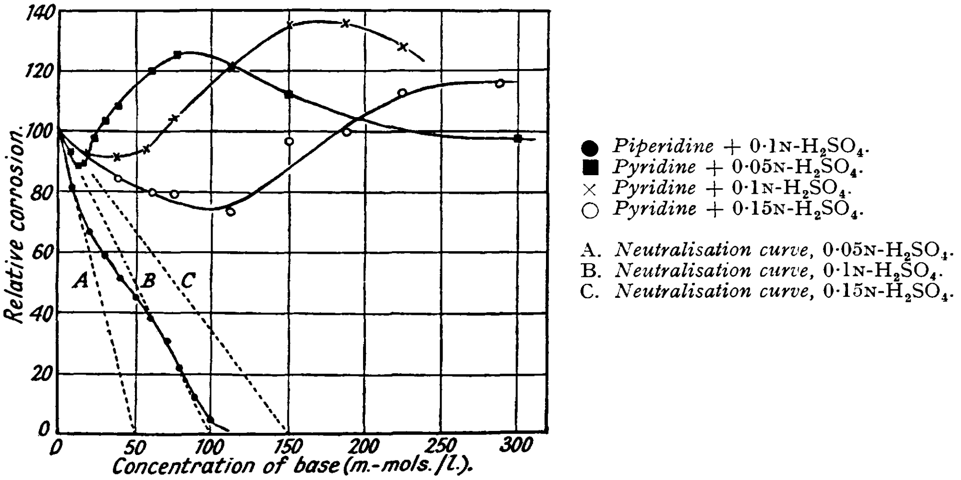
The apparent energy of activation is in all cases about 4000 cals./g.-mol. but shows a tendency to decrease with rise of temperature, for both the inhibited and the uninhibited reactions. There is also a sharp increase with the first increment of inhibitor, but with succeeding additions the energy decreases and approaches the value for the uninhibited reaction.

FIG. 4.

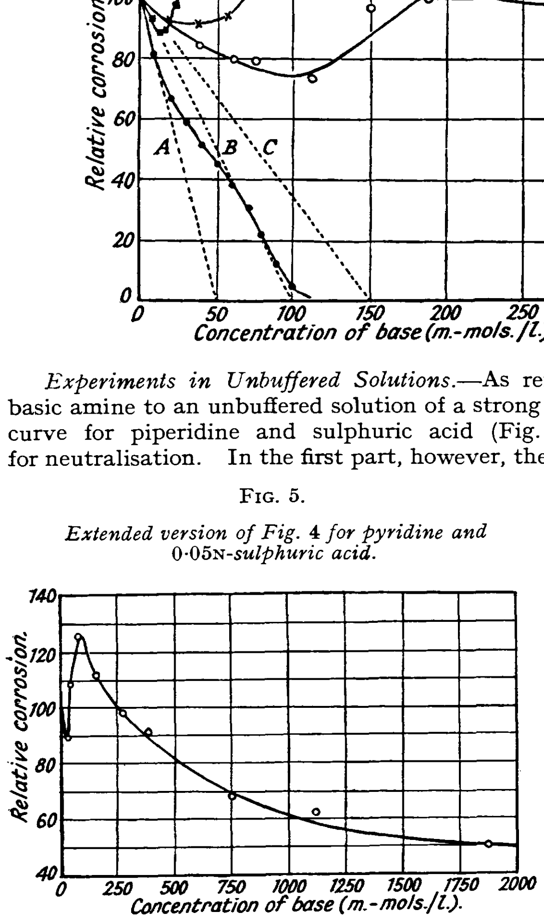
Effect of adding pyridine and piperidine to unbuffered acid solutions.



Experiments in Unbuffered Solutions.—As remarked earlier, the chief effect of adding a basic amine to an unbuffered solution of a strong acid is neutralisation. Thus the experimental curve for piperidine and sulphuric acid (Fig. 4) follows generally the theoretical curve for neutralisation. In the first part, however, the rate is always less than the theoretical, owing to the effect of the concurrent adsorption, but at the point of complete neutralisation, there is still a residual reaction equal to 4·6% of the original rate, showing that the piperidinium cation itself is acting as an " acid " in the extended sense.

FIG. 5.

Extended version of Fig. 4 *for pyridine and* 0·05N-*sulphuric acid.*



The experimental curves for pyridine show this effect even more clearly (also on Fig. 4). At the neutral points for three acid strengths it was found that the resulting pyridinium sulphate was more corrosive than the original sulphuric acid. Results obtained on adding extremely large amounts of pyridine to 0·05N-sulphuric acid are shown in Fig. 5.

Even when the solution was 1·8M. with respect to the pyridine, the reaction rate was still 50% of the uninhibited rate. Thus both faintly acid (pyridinium sulphate) and faintly basic (pyridinium sulphate and pyridine) solutions, show high reactivity, and this can only be interpreted as showing that the pyridinium ion itself is active in the metallic dissolution process. The curves of Fig. 4 and 5 therefore show the following effects: (*a*) initial neutralisation combined with slight inhibition, (*b*) a corrosive action by pyridinium ions which rises as the pyridinium ion/hydrogen ion ratio rises, (*c*) inhibition of pyridinium-ion corrosion by increasing amounts of pyridine. The complex nature of the interactions allows only general conclusions to be drawn and it is not yet possible to explain the shape of the curves in detail.

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