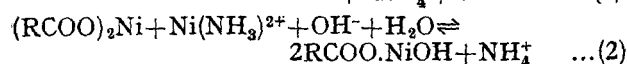
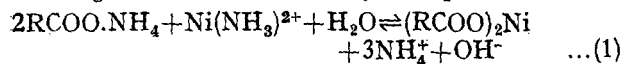


7.5 through a column (0.5×4.0 cm) of 1.0 g of the exchanger (5.93 meq.) and analysing 50 ml fractions of the effluent for the nickel content, till the effluent concentration reaches that of the influent. It is interesting to note that the nickel sorbed, by the breakthrough, is more than the capacity of the exchanger. Also the curve consists of two steps (curve 1, Fig. 1). The column was then washed with water. The sorbed nickel was eluted with 34.2 meq. of hydrochloric acid, followed by water till free of acid. This effluent contained 23.1 meq. of free acid and 10.28 meq. of Ni<sup>2+</sup>. Since the excess acid (5.17 meq.) consumed over that required for regeneration of the exchanger into H<sup>+</sup> form (5.93 meq.) is nearly equal to half the meq. of nickel eluted, it is concluded that nickel is present mostly as NiOH<sup>+</sup> by the time the exchanger is nearing exhaustion. Considering this data and the two steps in the sorption profile, it is inferred that nickel is initially sorbed as Ni<sup>2+</sup>, which transforms to NiOH<sup>+</sup> with increase of loading. This may be considered as an example of site-sharing on a cation exchanger. The reactions may be represented thus:



When 7.0 meq. of Ni<sup>2+</sup> at pH 7.5 were equilibrated with 2.70 meq. of the exchanger, it was observed by a similar analysis of the exchanger that 1.71 and 0.78 meq. of Ni<sup>2+</sup> were sorbed as Ni<sup>2+</sup> and NiOH<sup>+</sup> respectively. This lends further support for the transformation of Ni<sup>2+</sup> species to NiOH<sup>+</sup> species with increase of loading.

When the exchanger of the same capacity was taken in Na<sup>+</sup> form, 11.22 meq. of Ni<sup>2+</sup> was sorbed, showing the formation of NiOH<sup>+</sup> species to a greater extent than on NH<sub>4</sub><sup>+</sup> form of the exchanger. This is due to the greater tendency of RCOO.Na to hydrolyse and provide a higher concentration of OH<sup>-</sup> than RCOO.NH<sub>4</sub>.

Though sorption of nickel was decreasing with increase of NH<sub>4</sub><sup>+</sup> concentration in the solution phase (as expected), sorption of 75% and 60% of 2.0 and 0.5 mg of nickel taken was observed in batch experiments in the presence of 2.0 g of ammonium chloride in 100 ml at pH 7.5, when equilibrated with 0.25 g of exchanger. Nickel can, therefore, be recovered almost quantitatively from spent catalysts by employing the exchanger columns in series. Desorption of nickel with formic acid (curve 2, Fig. 1) was found to be as efficient as hydrochloric acid. This gives nickel formate for obtaining the active catalyst.

Similar experiments with a sulphonic acid exchanger (Dowex 50×8, NH<sub>4</sub><sup>+</sup>) revealed the sorption as well as desorption to be considerably less efficient, proving the greater advantage of a weak cation exchanger for the recovery of nickel.

The authors are grateful to Dr M. Sankar Das and Shri P. Murugaiyan for useful discussions.

#### References

1. SHKORBATOVA, T. L. & RYZHOVA, L. I., *Chem. Abstr.*, **66** (1967), 117992d.

2. GULYAeva, E. I., *Chem. Abstr.*, **54** (1960), 5986i.
3. GILMORE, A. J., *Chem. Abstr.*, **74** (1971), 115653k.
4. KALOC, J., *Chem. Abstr.*, **53** (1959), 17388a.
5. LAZAREV, A. I. & LAZAREVA, V. T., *Zavodskaya Lab.*, **25** (1959), 1301; *Chem. Abstr.*, **54** (1960), 8414h.
6. YATSUK, V. V., GETSKIN, L. S., LYSENKO, V. I. & PANTELEEVA, A. P., *Chem. Abstr.*, **69** (1968), 108850r.
7. YATSUK, V. V., LYSENKO, V. I. & GETSKIN, L. S., *Chem. Abstr.*, **69** (1968), 108849x.
8. WELCHER, F. J., *The analytical uses of ethylenediamine-tetracetic acid* (D. Van Nostrand, New York), 1958, 234.
9. SANDELL, E. B., *Colorimetric determination of traces of metals* (Interscience, New York), 1959, 668.

### Corrosion Inhibition Characteristics of Some Furan Derivatives from Their Quantum Chemical Values

AMARNATH MAITRA

Chemistry Department, University of Delhi, Delhi 110007

Received 20 October 1976; accepted 14 December 1976

Quantum chemical values such as ionization potentials and electron affinity of some furan derivatives have been successfully correlated with their corrosion inhibition characteristics in acid dissolution of iron.

FURAN derivatives have been used as corrosion inhibitors in the anodic dissolution of iron<sup>1</sup>. Vosta and coworkers<sup>2,3</sup> have correlated the quantum chemical parameters of a series of structurally related compounds with their corrosion inhibition characteristics. This paper reports a correlation between some quantum chemical parameters<sup>4</sup> such as ionization potentials and electron affinities of furan and some of its derivatives with their corrosion inhibition characteristics.

A cylindrical piece of iron (99.99% pure) mounted on teflon holder was used as the electrode. The electrode surface was polished successively with 150, 250, 360, and 600 emery papers and degreased with acetone and dried. Disc surface (0.2 cm<sup>2</sup> area) was exposed to the solution and satisfactorily tight seals were provided between iron surface and teflon. Triply distilled water was used. Furan, furfurylamine and furic acid were of AR grade and used as such.

The galvanostatic method used for steady state polarization studies consisted of a constant current generator and one vernier potentiometer having different channels for measuring corrosion current and corrosion potentials. All experiments were carried out at 25±0.1°. Corrosion rates were measured in terms of log *i*<sub>corr</sub> (current density) in 1M perchloric acid containing 0.1M inhibitor solution.

The relation between inhibition characteristics and quantum chemical data shows that log *i*<sub>corr</sub> mostly depends upon the energy of the highest occupied molecular orbital (HOMO) which is a theoretical analogue to the ionization potentials of a substance. The lowest free molecular orbital (LFMO) which gives idea about electron affinity of the molecule is also shown to be dependent on the log *i*<sub>corr</sub> values (Fig. 1). It is observed that the inhibition characteristic increases with increase in the energy of HOMO, i.e. with decrease in ionization potential. Thus the inhibition effi-

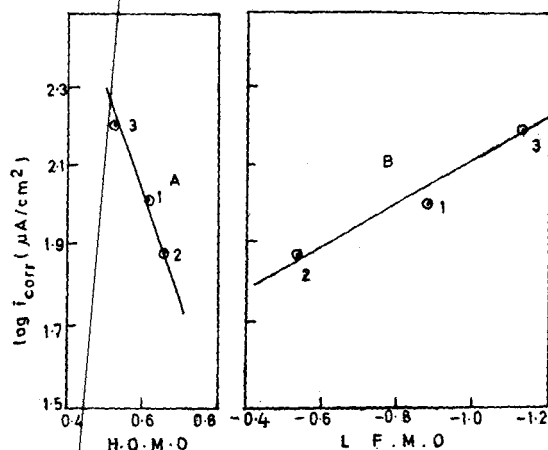


Fig. 1—Dependence of HOMO (curve A) and LFMO (curve B) of inhibitors on  $\log i_{corr}$  [1, furan; 2 furfurylamine; and 3, furoic acid]

ciency increases with the ease of ionization of the molecule. This implies that the molecule is acting as an electron donor when it is adsorbed over the metal surface and thus retards corrosion. Furan lies between furfurylamine and furoic acid in corrosion inhibition properties, indicating that electron density on the heterocyclic oxygen atom is the determining factor for the inhibition effect. Carboxylic group in furoic acid reduces the electron density over cyclic oxygen atom whereas methylene-amino group, due to hyperconjugative effect and inductive effect, increases it. This presumption is to some extent, corroborated by the dependence of energy of LFMO orbitals upon  $\log i_{corr}$  (Fig. 1) This correlation shows that efficient inhibitors are bad acceptor of electrons. On the other hand it may be remarked that easily reducible compounds stimulate corrosion instead of inhibiting it.

The author thanks Dr J. Nagchoudhuri for her kind help in HMO calculations.

**References**

1. VAIDYANATHAN, H. & HACKERMAN, N., *Corros. Sci.*, **11** (1971), 737.
2. VOSTA, J. & ELIASEK, J., *Corros. Sci.*, **11** (1971), 223.
3. VOSTA, J. & ELIASEK, J., *Werk. Korros.*, **23** (1972), 487.
4. STREITWEISER, A. (Jr), *Molecular orbital theory for organic chemists* (John Wiley, New York), 1961, 117.

**Studies on the Oxidation of Propylene by Zinc Molybdate**

T. K. VARADARAJAN, B. VISWANATHAN & M. V. C. SASTRI\*

Department of Chemistry, Indian Institute of Technology Madras 600036

Received 9 August 1976; accepted 8 February 1977

The kinetics of the oxidation of propylene over a zinc molybdate catalyst have been studied in the temperature range 350 to 410°C with the variation of propylene and oxygen partial pressures, using a differential flow-type reactor. The reaction has been found to be first order with respect to propylene and zero order with respect to oxygen partial pressure.

\*Present address: Head, Materials Science Research Centre, Indian Institute of Technology, Madras 600036.

**M**OLYBDATES as catalysts, particularly for the oxidation of propylene to acrolein have attracted considerable attention. In the present case, the oxidation of propylene on a zinc molybdate catalyst has been taken up with a view to studying the kinetics of oxidation as well as to characterize the activity of the catalyst.

The oxidation has been studied using a flow-type differential micro-reactor in the temperature range 350 to 410°. The preparation of zinc molybdate catalyst and its physical characterization have been described in our earlier paper<sup>1</sup>. The purity of propylene, obtained by dehydrating pure distilled isopropyl alcohol over alumina catalyst at 350°, has been checked by gas chromatograph. Nitrogen gas has been used as a diluent along with the reactant gas mixture, oxygen and propylene.

Keeping the total flow rate constant at 140 ml/min as well as that of propylene at 45 ml/min, the flow rate of oxygen has been varied from 25 to 80 ml/min at 350° and from the constant percentage conversion of propylene (~7.5%) at various flow rates of oxygen, it has been deduced that the reaction is independent of the oxygen partial pressure, i.e. the reaction is zero order with respect to oxygen. In order to evaluate the order with respect to propylene, the percentage conversion of propylene has been evaluated at three different temperatures with various flow rates of propylene.

The plot of  $[-\log(1-x)]$  vs reciprocal space velocity (Fig. 1) has been found to be linear at all the three temperatures, thus showing that the reaction is first order with respect to propylene. From the rate values, the activation energy for the reaction has been found to be 9.3 kcal/mole.

The major detectable products formed from the oxidation of propylene on  $ZnMoO_4$  are acrolein, water and carbon dioxide. The catalyst has been found to possess considerable activity (60% selectivity) for partial oxidation of propylene to acrolein.

Carbon dioxide can be formed either by direct combustion of propylene or by oxidation of acrolein or through any other intermediate species that may be obtained during the oxidation. The percentage carbon dioxide formed at various contact times and temperatures (Table 1) has been found to be almost constant throughout, thus showing that (i) the

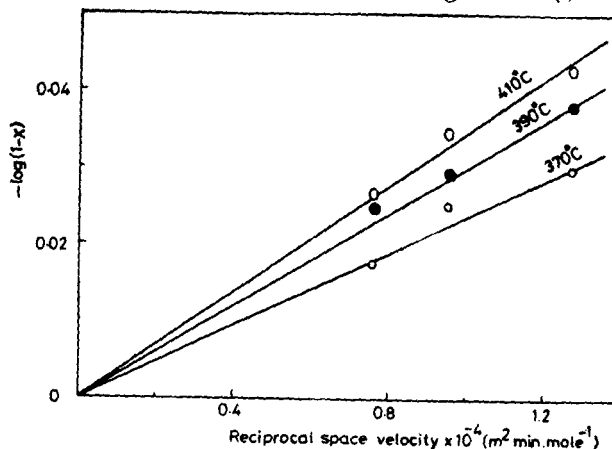


Fig. 1—Plot of  $-\log(1-x)$  vs reciprocal space velocity  $\times 10^{-4}$  ( $m^2 \text{ min mole}^{-1}$ )