preponderantly unsymmetrical compounds, because their synthesis hinges directly or indirectly on addition of a hydrogen halide to a double bond; for instance, fluorination of symmetrical $CHCl_2$-$CHCl_2$ with antimony trifluoride or hydrogen fluoride leads to asymmetrical CHF_2CHCl_2, then CF_3CH_2Cl.[5]

In each reaction, it was noted that some low boiling material was invariably present. This was taken as an indication that some halogen substitution had taken place, probably at the expense of the lead difluoride, and should be investigated further as it may lead to a more efficient utilization of the total fluorine available in the reaction.

In addition to the reactions listed in the table, one diene was subjected to the lead dioxide and hydrogen fluoride treatment. Perchlorobutadiene $CCl_2{=}CClCCl{=}CCl_2$, $n^{20}{}_D$ 1.5542 gave a reaction product with a refractive index of 1.492 and an analysis which corresponded to a formula $C_4Cl_6F_2$ (Cl: found 69.6%, calcd. 71.2%). This compound discolored permanganate, and can therefore be represented by only two formulas, $CFCl_2$-$CClFCCl{=}CCl_2$ or $CFCl_2CCl{=}CClCFCl_2$, which correspond to the fluorination of only one of the two double bonds, by 1,2- or by 1,4- addition, respectively. This difluoride reacted readily with zinc, with the loss of chlorine only, a fact which seems to favor the first formula.

Summary

Addition of fluorine to an olefinic double bond has been achieved by interaction of lead dioxide with hydrogen fluoride in the olefin which is to receive the fluorine. The reaction makes nascent lead tetrafluoride, which decomposes into lead difluoride and a mole of fluorine which is accepted by the olefinic double bond.

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(5) Henne and Renoll, THIS JOURNAL, 58, 887 (1936).

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY OF IDAHO]

Activation of Passive Iron in Chromic–Sulfuric–Nitric Acid Solution by Rapid Rotation

BY W. H. CONE AND DON H. ANDERSON

The existence of passive iron was reported over one hundred and fifty years ago. Passivity is an intriguing phenomenon and one of fundamental importance. Each year a new series of papers with new approaches to this problem appears. Much disagreement exists among various investigators and probably will continue until it is recognized by all that passivity may be due to a number of factors and that it may be destroyed in many ways.

There are certain important points on which most investigators agree: one, that the passivating agents, whatever they may be, are capable of depositing on a piece of iron a film whose exact nature is unknown; second, a sample of passive iron tends to lose its passivity at higher temperatures in passivating solutions; third, most passivating agents are oxidants; fourth, any condition which can destroy the protective film is capable of causing activation.

It was shown[1] that iron could be made active in chromic acid solutions by reducing the pressure before immersing the iron in the solution. It was believed that the primary cause of passivity was an adsorbed layer of oxygen on the iron and that the reduction in pressure altered this layer to such an extent that the chromic acid was able to attack the metal. Since no gas was evolved in this reaction, no gas film could be formed and once active the iron continued to dissolve.

Experimental

The solution had the composition: CrO_3 51.0%; H_2SO_4 6.3%; H_2O 42.2%; HNO_3 0.5% and is hereinafter called the chromic acid solution. The chemicals were all analytical reagent grade. The iron rod in most of the experiments was a soft commercial iron having a diameter of 5 mm. and a length of 120 mm. However, a few check runs were made using J. T. Baker Co. "Iron Wire for Standardizing" which was wound around a glass rod to give rigidity. The vessel containing the solution was provided with two side arms for insertion of a potassium nitrate–agar bridge and a thermometer. The potential of the rod was measured against a normal calomel half cell. Immediately before each run the rod was polished with fine emery paper. Runs were made by placing the rod in the chromic acid solution and increasing the speed of the motor until the potentiometer reading indicated that the iron was active.

The speed of the rotating rod was determined either by a tachometer or by a stroboscope.

The rotational speed necessary to produce activation appears to be dependent on the turbulence in the solution. The data for a smoothly rotating rod are shown in Table I and curve A in Fig. 1.

TABLE I

ACTIVATING SPEED FOR ROD RUNNING ON CENTER

Temp., ° C.	5.0	12.0	22.4	25.5
R. p. m.	12200	11900	8100	8600
Temp., ° C.	26.0	26.5	34.0	37.8
R. p. m.	8140	7690	7675	6400

The data in Table II and Curve B, Fig. 1, are for a rod bent so that the moving tip was 2 mm. offset from the axis of rotation. This produced considerable turbulence in the solution and caused activation at considerably lower speeds.

TABLE II

ACTIVATING SPEED FOR ECCENTRIC ROD

Temp., ° C.	1.0	5.5	8.1	8.9	11.1	15.2	19.8	22.1
R. p. m.	4450	4600	4740	4400	4030	2620	2940	3250
Temp., ° C.	23.2	23.3	26.2	27.1	27.5	28.7	29.1	31.0
R. p. m.	3290	3300	2925	2890	2820	2750	2700	2650

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(1) Cone and Tartar, THIS JOURNAL, 59, 937 (1937).

Discussion

While the data presented are not entirely concordant, they show that iron can be made active by rotation. The rotational speed, temperature, surface condition of the rod, and turbulence of the solution are the primary factors that must be considered. Another factor that must be considered is the presence of halide and other ions that have a marked effect on the ease of activation as shown by Cone and Tartar.

Samples of C. P. iron wire were made active by holding them in a chamber which was evacuated with a Cenco Hyvac pump before admitting the chromic acid solution. Samples that were not so treated before being placed in the solution were passive. No attempt was made to determine transition pressure for this system.

An attempt was made by Crog and Hunt[2] to make the iron active by a reduction of pressure. They were unsuccessful. We are unable to account for their failure. However, our experience has been that best results are obtained in solutions having a higher concentration of CrO_3 than was used by Crog and Hunt. The suggestion made by them that diffusion of halide from the half cell might have been responsible for the activation is untenable, as a potassium nitrate–agar bridge was used. Slight changes in nitrate concentration produced by diffusion would be insignificant when compared with the amount of nitric acid in the solution. Furthermore, many trials were made in which no half cell was introduced into the system until after activation occurred.

It is possible to express the variation of the critical activating speed (V_c) with temperature in equation form and the two equations A and B are derived from the corresponding data.

$$t = 66 - 0.00476 V_c \qquad \text{(A)}$$

$$t = 62 - .0124 V_c \qquad \text{(B)}$$

It is evident that there is a temperature at which activation should occur when V_c equals zero and the two calculated temperatures are 66 and 62°, respectively.

In order to determine this transition temperature, the rod was placed in a stoppered flask in contact with chromic acid solution and warmed. It was observed that the rod became active at 63° for one trial and 65° in a second trial.

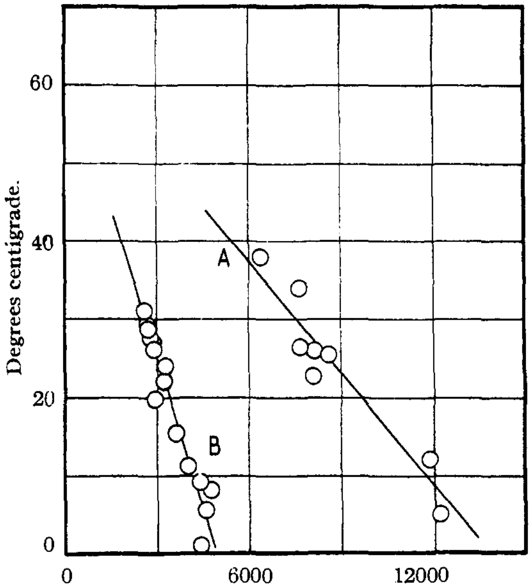

Fig. 1.

Acknowledgment.—The authors wish to acknowledge assistance received from Edgar Stockton and George Sprague, who made some preliminary investigations on this problem.

Summary

Iron rods that are passive can be activated by rotation in solutions containing a high concentration of CrO_3 with some sulfuric acid and nitric acid present.

A rise in solution temperature has a marked effect in lowering the activating speed.

Turbulence and/or vibration apparently is a factor in the activation process.

The passivity disappears at about 64° and this value is in excellent agreement with the extrapolated values obtained from the rotation measurements.

This seems to support previous work indicating the existence of an adsorbed gaseous film of unknown composition as the primary cause of passivity of iron in this solution.

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[2] Crog and Hunt, *Trans. Electrochem. Soc.*, **79**, 145 (1941).