

times more susceptible to cleavage by γ -radiation⁸ (G 2.4). It is clear that protection by aromatic groups, as described here, offers a useful practical method of reducing the radiation lability of carbohydrates and demonstrates that facile energy transfer is possible in these molecules.

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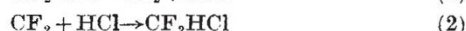
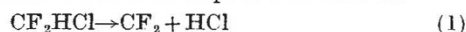
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Pyrolysis of Chlorodifluoromethane and the Heat of Formation of Chlorodifluoromethane and Difluoromethylene

In a recent communication by Gozzo and Patrick¹ the heat of formation of difluoromethylene was estimated at ≤ -43 kcal/mole from an investigation of the kinetics of pyrolysis of chlorodifluoromethane. We completed a similar investigation of this pyrolysis in the range 530°–700° C some time ago and obtained slightly different results (to be submitted for publication elsewhere). We believe that the main reaction steps are as follows:



The inhibiting effect of HCl (that is, reaction 2) was confirmed by copyrolysis of CF_2HCl and HCl. Further, pyrolysis of a mixture of CF_2HCl with HBr led to CF_2HBr as the main product. Reaction 4 was inferred from the reversibility of the overall reaction:



The function $p(\text{C}_2\text{F}_4)/p^2(\text{HCl})/p^2(\text{CF}_2\text{HCl})$ has the form of an equilibrium constant, and in static system investigations at 600° C this function was found to increase with time and attain a maximum value, after which it fell slowly because of the formation of side products. It was possible to extrapolate the curve and make an estimate of what the final value of the function would have been had there been no side reactions. A value of 8.7×10^{-2} atm. was obtained. Published thermodynamic data^{2,3} lead to a value of 30.1 cal/mole deg for ΔS° for reaction (5) and hence to a value of 30.5 kcal/mole for ΔH° , at 600° C, which corresponds to $\Delta H^\circ = 29.1$ kcal/mole at 25° C. If the heat of formation of tetrafluoroethylene is taken as -151.5 kcal/mole, this leads to a value of -112.3 kcal/mole for the heat of formation of chlorodifluoromethane at 25° C, which is close to several recent estimates^{1,4–6}.

Arrhenius parameters were obtained for reactions 1, 2, 3 and 4 by using a computer to integrate the kinetic equations and to obtain a least-squares fit to the experimental results obtained in a flow system at 1 atm. over the range 530°–700° C. Use was made of available thermodynamic data, including the heat of reaction (5) estimated as indicated, to minimize the number of independent

parameters to be found, and E_3 was assumed to be zero. An empirical expression was used to take account of the formation of by-products (which have been described by Park⁷); the amount formed rarely exceeded a few per cent.

The Arrhenius parameters found in the least-squares procedure mentioned were (in kcal, litre, mole, sec units) $A_1 = 10^{13.84}$, $A_2 = 10^{8.35}$, $A_3 = 10^{9.94}$, $A_4 = 10^{16.66}$, $E_1 = 55.8$, $E_2 = 6.2$, $E_3 = 0$ (assumed), $E_4 = 70.4$. From these data, a value of -39.1 kcal/mole for the heat of formation of CF_2 at 25° C is obtained; this is in reasonable agreement with various recent estimates^{1,4}.

When E_3 was introduced as a further adjustable parameter into the least-squares fitting instead of being assumed zero, a value of about 5.8 kcal/mole was obtained, but this was very badly determined and did not exceed its own uncertainty. The corresponding heat of formation of CF_2 was -46.3 kcal/mole.

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Inhibition of Corrosion of Iron in Chromic Acid

CORROSION of iron is completely inhibited in 0.1 N chromic acid of pH 1.4, but a loss of 4 000 mg/dm² was recorded on iron in 0.1 N sulphuric acid of pH 1.6 after immersion for 4 weeks. Film thickness and time-potential measurements indicated the oxide film on iron to be more protective in chromic acid than sulphuric acid.

The electrode potential of iron in chromic acid after 24 h fluctuates from +0.4 to +0.5 V (hydrogen scale), while that in sulphuric acid after 24 h is -0.36 V.

The oxide film thickness increases from 12 Å to 22.5 Å after 24 h in chromic acid, but decreases from 6 Å to values ≤ 5 Å after 24 h in sulphuric acid. Contact of bulk $\alpha\text{-Fe}_2\text{O}_3$ and Fe_3O_4 with the acids for 1 h caused the dissolution of 0.5 p.p.m. of iron from $\alpha\text{-Fe}_2\text{O}_3$ and 13 p.p.m. of iron from Fe_3O_4 in each acid. After 24 h the corresponding figures were 7 and 100 p.p.m. respectively in chromic acid, and 9 and 50 p.p.m. in sulphuric acid.

Measurement of the rate of solution of iron from oxide-covered iron showed 0.7 p.p.m. of iron dissolved from 90 cm² of iron in 200 ml. of chromic acid solution after 1 h, while 15 p.p.m. dissolved in sulphuric acid. Contact of iron powder with chromic acid produced chromic ion: 0.5 p.p.m. of chromium was irreversibly absorbed from 200 ml. of chromic acid on to 90 cm² of iron after immersion for 1 h.

The electrochemistry of iron was investigated in chromic and sulphuric acids using a potentiostat (Fig. 1). After reduction of the oxide film on iron by application of a cathodic current of 40 m.amp/cm² for 2 min.—7.5 mc./cm² is required to reduce the oxide film on iron¹—the potential of the iron electrode was increased, readings being taken at 2-min intervals. Results obtained in sulphuric acid showed no evidence of film formation involving ferrous oxide formation until an anodic current of 24 m.amp/cm²