FLUORINE ATOMS FROM AN R.F. ELECTRIC DISCHARGE

By R. J. McIntyre* and F. K. McTaggart*

[Manuscript received July 26, 1971]

We have previously reported the production of atomic chlorine, bromine, and iodine, in a 28-MHz electric discharge and distinguished these from their parent molecules by their different tarnishing reaction with silver.[1] We have now also done this with fluorine.

Dry fluorine diluted 1 : 1000 with argon was passed over two polished silver samples in a fast-flow vacuum system.

The gas flow passed through a discharge produced by a 28-MHz oscillator before reaching the second sample. The rate of growth of films of silver fluoride on the surface of the silver was followed by recording the variation in the intensity of a beam of monochromatic light reflected from the surface. Changes in intensity occur due to interference between rays reflected from the film and from the film substrate, during growth. The optical system used has been described previously.[1] The flow system was made of Pyrex glass and no "wall poison" was used.

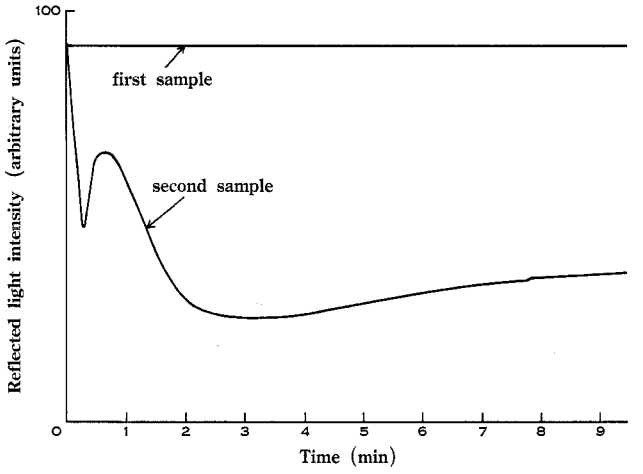

Fig. 1.—Recordings of reflected light intensity from silver surfaces during attack by fluorine at 24°. The first sample was upstream from the discharge and the second sample 7 cm downstream from the visible discharge.

At room temperatures using flow rates of 400 ml/hr s.t.p. and pressures of 0·25 mmHg, no visible film was observed on the upstream sample whilst a light brown film formed on the downstream sample. The film was uniform in appearance and gave interference curves during formation (see Fig. 1). The increase in film

* Division of Mineral Chemistry, CSIRO, P.O. Box 124, Port Melbourne, Vic. 3207.

[1] McIntyre, R. J., and McTaggart, F. K., *J. phys. Chem.*, 1970, **74**, 866.

thickness corresponding to a change in light intensity from a minimum to a maximum was 660 Å; owing to the opacity of the film, the thickness could only be monitored to approximately 2000 Å. The film deliquesced rapidly on removal from the tube. At higher temperatures (*c.* 100°C) films were also formed on the upstream sample but were still too thin to exhibit interference effects, i.e. less than about 600 Å; these were also deliquescent.

The enhanced rate of growth of films downstream from the discharge was attributed to atomic fluorine produced in the discharge.[2]

It was concluded that fluorine is similar to chlorine in that it forms a highly protective film at room temperature but that the atomic species are able to penetrate the silver halide film more readily. However, unlike the other atomic halogens which form silver halide films at linear growth rates, atomic fluorine produces films of silver fluoride in accordance with a direct logarithmic rate law of the form

$$W = K \log(at+1)$$

where W is the film thickness at time t, and a and K are constants.

The initial rate of film growth corresponds nearly to the maximum which could be obtained if all the fluorine present reacts. This implies a high degree of dissociation of fluorine in the discharge and a high reaction probability (approaching unity) for fluorine atoms.

[2] Rosner, D. E., and Allendorf, H. D., *J. phys. Chem.*, 1971, **75**, 308.