FORMATION OF HF IN THE MERCURY-SENSITIZED PHOTOLYSIS OF FLUOROHYDROCARBONS

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Summary

A previously described technique (Heckel and Marsh) for analysis of nanomolar quantities of fluoride ion involves potentiometric titration of F^- with La^{3+} in ethanol–water mixtures. Modification of the method by the addition of millimolar Cl^- allows accurate measurement of fluoride even in the presence of Hg/Hg^{2+}. Using this approach, HF formation was followed during the Hg $6(^3P_1)$ sensitized photolysis of the three systems CH_3CH_2F, CH_3CHF_2, and CH_3CF_3. Resulting HF yields fell in the order $HF(CH_3CH_2F)$ $> HF(CH_3CHF_2) \gg HF(CH_3CF_3)$, consistent with mechanistic assumptions of Scott and Jennings.

Introduction

Hydrogen fluoride is either known or postulated to be a major product in the radiolysis [1, 2], photolysis [2], and Hg $6(^3P_1)$ sensitized photolysis [3, 4] of partly fluorinated hydrocarbons. However, in most of the decomposition studies of such fluorohydrocarbons, the yield of HF is not directly measured [1 - 4]. A potentiometric titration method for the determination of small (sub-micromole) amounts of HF formed in such decomposition experiments is available and is known to be accurate [5, 6]. This method of analysis cannot be used directly for the measurement of HF in the presence of mercury ions and mercury, since fluoride ions complex with mercury ions. Hence, a simple modification of this method was devised to overcome this difficulty. It was found that addition of small amounts of chloride ions to the analyte release the complexed fluoride ions.

The mercury sensitized photolysis of partly fluorinated ethanes has been investigated [4]. This is one of the systems where HF is postulated to be a major product even though a direct analysis was not carried out. The mechanisms postulated to explain the formation of organic products rely heavily on the formation of HF as a major product. Hence, we undertook the mea-

surement of HF in the Hg $6(^3P_1)$ sensitized photolysis of C_2H_5F, $1,1\text{-}C_2H_4F_2$, and $1,1,1\text{-}C_2H_3F_3$.

Experimental

The photolysis set-up and procedures are described in detail elsewhere [7, 8]. A General Electric 15 W Germicidal lamp (type G15T8) was used as a source of 253.7 nm radiation, and a quartz vessel equipped with a mercury saturator was used as a photolysis cell. The reagent gases, ethyl fluoride, 1,1-difluoroethane, and 1,1,1-trifluoroethane were obtained from Peninsular Chem. Research, Matheson, and Air Products, respectively. All the reagents were subjected to at least 10 freeze—pump—thaw cycles to remove air from the samples.

Hydrogen formed in the photolysis was determined by pumping the products non-condensible at −196 °C using a Toepler pump into a McLeod gauge where it was measured. The organic products were measured using a Tracor 550 Research gas chromatograph equipped with a flame ionization detector. A 4.6 m (Analab) silica gel column with the carrier gas was used.

Preparatory to a wet-chemical analysis of HF, an extractant solution of 2 ml of 66% ethanol in water was introduced into the tube extending beyond the break-seal on the photolysis vessel. With the cell contents frozen, the break-seal was opened with a rod introduced through a piece of rubber tubing used as a gland. This procedure was necessary to avoid condensation of oxygen inside the vessel. The vessel was warmed to room temperature and the ethanolic solution was left in contact with the walls of the vessel for at least 30 minutes to extract all the fluoride ion into the solvent. This solution was transferred into a 5 ml polyethylene beaker, and the vessel was rinsed out into the beaker with another 2 ml of 66% ethanol.

The determination of HF was based on a previously described electro-chemical procedure [6]; however, it was necessary to make a minor modification to permit analysis in the presence of mercury or mercuric ions. A drop of dilute aqueous NaCl was added to the fluoride ion solution prepared as described above.

To make sure that the added chloride ion was not interfering with the fluoride ion determination, a series of experiments using known amounts of NaF was carried out. (The Orion fluoride ion selective electrode, model 94-09, used in these experiments is claimed to have a selectivity of 1000:1 over chloride ions [9].) In these verification experiments 40 μl of 5.00×10^{-3} M NaF was titrated against 5.00×10^{-3} M La(NO$_3$)$_3$ solution, in the presence of chloride ion and/or mercuric ion and mercury. Figure 1 shows the titration curves for these analyses. In case of the titration in the presence of mercuric ions, the e.m.f. changed from −0.052 V to −0.003 V soon after the addition of mercuric ion indicating the complexation of fluoride ions with mercuric ions; the subsequent addition of chloride ion changed the e.m.f. back to −0.051 V, indicating the release of fluoride ion into the solution.
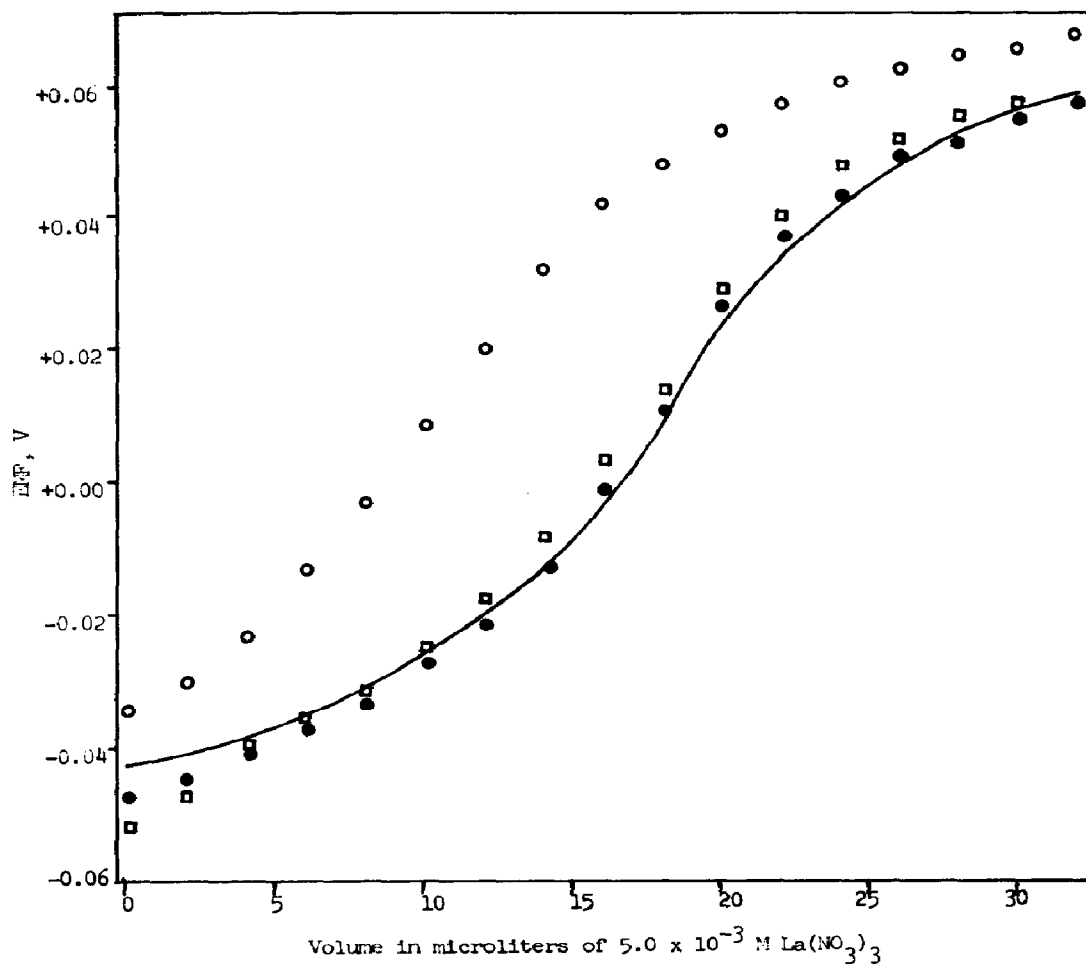
Fig. 1. Titration curves for quantitative analysis of F^- ion: □, 40 μl of NaF + Hg^{2+} ion + Cl^- ion; ●, 40 μl of NaF + Cl^- ion; ———, 40 μl of NaF; ○, photolysis.

These experiments show that the chloride ions (which can be used to release fluoride ions from mercuric ions) do not interfere with the determination of fluoride ions.

In all these experiments, the procedure prescribed by Heckel [6] was followed. It was essential to condition the fluoride ion selective electrode by performing at least two titrations using this electrode before it could be used for a quantitative determination. During all the titrations, the analyte was continuously stirred using a magnetic stirrer, and the e.m.f. was monitored using a high input impedance (10 MΩ) Hickock digital volt–ohm meter.

Results and Discussion

The yield of HF in three partly fluorinated ethanes, C_2H_5F, $1,1\text{-}C_2H_4F_2$, and $1,1,1\text{-}C_2H_3F_3$, was measured as a function of photolysis time. The yield —
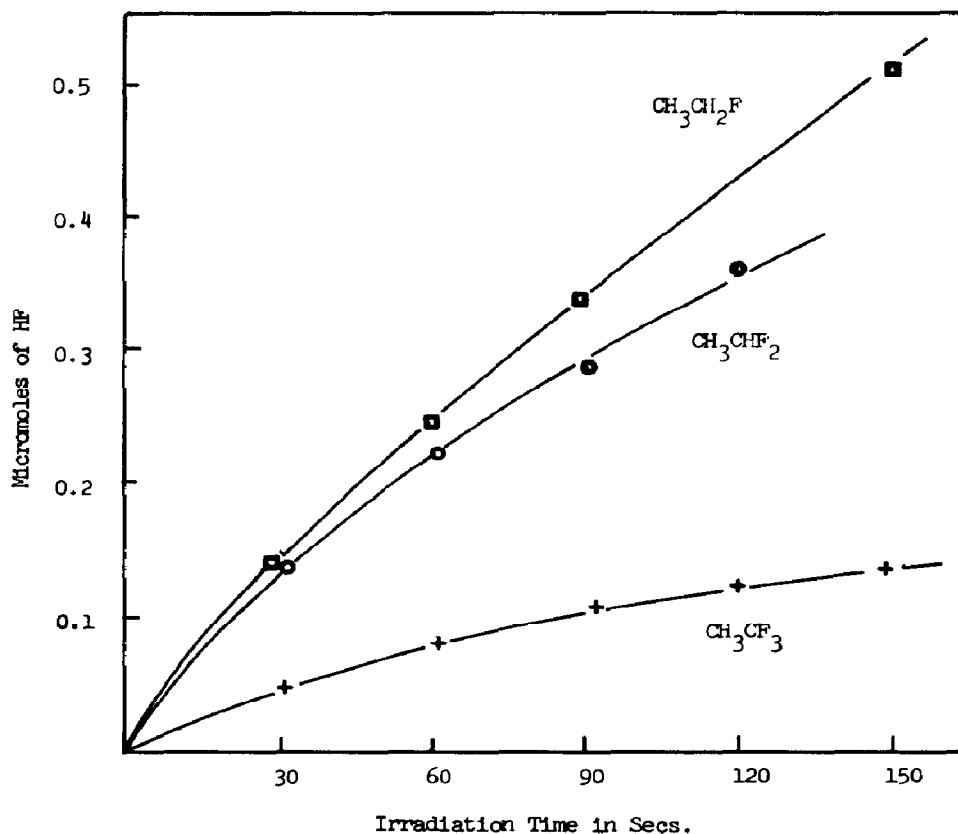
Fig. 2. Yield of HF as a function of time in the photolysis of 50 Torr samples of C_2H_5F (□), CH_3CHF_2 (○) and CH_3CF_3 (+).

time plots are shown in Fig. 2. The yield of HF was maximum in C_2H_5F and minimum in CH_3CF_3. The ratio of H_2/C_2H_6 in the photolysis of C_2H_5F was measured to obtain a basis for comparison of our data with that of Jennings [4]. This ratio was measured to be 3.1 in our experiments. This value compared well with 2.95 which was obtained by Jennings [4]. Based on this ratio (2.95), the ratio of the yields of HF to that of H_2, and that of HF to C_2H_6 were calculated to be 1.02 and 3.02, respectively.

Using the measured yield of HF, the mass balance in the C_2H_5F system was calculated to be $C_2H_{4.4}F_{0.97}$. This is to be compared with $C_2H_{3.99}F_{0.57}$ which was calculated using Jennings' data. Obviously, the mass balance is considerably improved when the HF yield is taken into consideration. In the above calculation of mass balance, only the HF yield was taken from our experiments. However, we obtained more H_2 relative to C_2H_6, than did Jennings, which would lead to further improvement of the mass balance.

According to the model proposed by Jennings [4], Hg-sensitized photolysis of fluorohydrocarbons proceeds efficiently only when the molecule contains both fluorine and hydrogen on the same carbon atom. Quenching of the Hg $6(^3P_1)$ atom results in removal of an α-hydrogen, which can either

abstract hydrogen (again, at the α-position preferentially) or recombine with the parent radical, giving an excited intermediate which can either be deactivated or decomposed:

$$H\cdot + CH_3CHF\cdot \rightarrow CH_3CH_2F^* \tag{1}$$

$$CH_3CH_2F^* \quad \rightarrow CH_2{=}CH_2 + HF \tag{2}$$
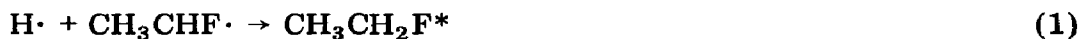
According to this model, sensitivity of CH_3CF_3 to decomposition in a Hg-sensitized photolysis experiment should be much less than that of either CH_3CH_2F or CH_3CHF_2, consistent with our results. However, the relative sensitivity of the monofluoro- and difluoro-compounds is not easily predictable. Consistent with Jennings observations, however, we found a greater sensitivity for the monofluoro compound.

In summary, we have described a method for HF analysis under the conditions of mercury-sensitized photolysis. The HF yields in partly fluorinated ethanes were studied as a test case and found to be in accord with expectations from previously published work.

Acknowledgements

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