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The Action of Elementary Fluorine upon Organic Compounds. XIX. A New Jet Fluorination Reactor

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An entirely new type of direct fluorination reactor has been developed which employs a highly turbulent jet of the diluted organic reactant and in which the fluorine is also well mixed with circulating reactor gases. The continuous vapor phase reaction takes place in an unpacked space, essentially without flame and at relatively low temperatures, to produce a high yield of perfluoroethane from ethane with very little cleavage or polymerization. This result is regarded as a significant step in the orienting of direct fluorination reactions toward specific products.

In a preceding paper[2] we have described the successful operation of a metal-packed direct fluorination reactor incorporating a concentric tube burner developed as a result of a study of fluorine diffusion flames. That study has now been extended considerably, and the results, which have led to a distinct advance in reactor design, are presented here. They also have led to a marked advance in the orientation of a direct fluorination reaction toward a single product, thus tending to eliminate the chief difficulty inherent in such fluorinations.

One of the most important features of the new reactor is that the actual fluorination takes place in an unpacked space; thus disposing of the problems associated with the nature and size of the packing grains, channeling, polymeric or carbonaceous deposits and the possible catalytic influence of the metal or metal halide coating involved. Proof that it was feasible to dispense with all packing was obtained when the test gas ethane was burned in fluorine in the unpacked burner reactor with the following striking results. At the fluorination ratio of 7:1, or enough to burn the entire sample to CF_4, with no dilution, and when the fluorine was admitted through an extension to the central ring causing it to circulate and become diluted with relatively inert reactor gases, while ethane came in through the outer ring at 0.08 mole/hr., there were formed: CF_4 60%, C_2F_6 22% and C_3F_8 6%. Not only this, but when the ethane was diluted with nitrogen so that the dilution ratio (N_2 in C_2H_6 to F_2) was 8:1, and using the cooler convection type flame as before, there were formed after condensation and rectification in the usual manner: CF_4 9%, transition 17%, C_2F_6 58% and C_3F_8 trace. This production of nearly 60% C_2F_6 without packing but in a flame and in the presence of an excess of fluorine has not been observed previously, and was considered especially noteworthy.

Perhaps the most significant characteristic of the new unit is the admission of the diluted sample under slight pressure through a highly turbulent jet. Even the cool flame mentioned above was still of the laminar diffusion type with a relatively hot flame front, at which cracking so often takes place either prior or subsequent to the expected reaction. In order to minimize this effect by producing a more homogeneous flame, it was decided to introduce turbulence into the system by the use of the jet. Then it was discovered that when the jet velocity exceeded the velocity of flame propagation the flame could be completely blown off, leaving in the upper part of the reactor a mixture of reacting gases which gave off a faint blue glow, and corresponded to a very mild and homogeneous type of fluorination with no flame front. In a trial run using a modified burner reactor with the jet attached to the central ring and the fluorine coming in far away at the base, at the fluorination ratio (F_2:C_2H_6) of 6:1, dilution ratio (N_2 in C_2H_6 to F_2) 10:1, ethane flow rate 0.04 mole/hr., there were obtained: forerun 3%, CF_4 *none*, C_2F_6 55%, CF_3CHF_2 11%, C_3F_8 none, residue 3%. Significantly this fluorination had produced neither cleavage nor chain building to any extent, while 92% of the recovered product consisted of C_2F_6 and CF_3CHF_2. Finally, the most turbulent practicable jet, which had a $^1/_{64}$″ orifice $^1/_{32}$″ long preceded by a much larger bore approximately $^1/_8$″ in diameter, as suggested by Dr. C. D. Fulton of the Duke Engineering School, was adopted for the new reactor in order to dilute the reactants beyond the kindling point at maximum speed. It also reduced the dilution ratio (N_2:F_2) necessary to blow out the flame from 10:1 to 2:1.

A third important detail of the new reactor is the use of a jet pump to increase the internal circulation greatly, in order to dilute the incoming fluorine very efficiently with relatively inert reactor gases. As noted above, such dilution already had been observed to moderate the reaction considerably in the unpacked burner reactor. Therefore in the new unit the jet was surrounded by a Meker tube having no grid but with the slots placed well below the orifice of the jet. This arrangement was so efficient that it was possible to reduce the dilution ratio (N_2:F_2) as low as 1:1 and still blow the flame off. However the rate of fluorination was so greatly reduced at the same time that the concentration of unreacted gases at the top of the unit began to build up to the ignition point, causing periodic mild explosions. Fortunately these could be completely prevented by electrically heating the top of the reactor to again increase the rate of fluorination there.

The foregoing are the three special features of the new reactor described in detail below.

The New Jet Reactor

This unit, which is illustrated to approximate scale in Fig. 1, consisted of a primary reactor A, and a secondary reactor B, connected in series with it. Reactor A was made from a section of brass pipe 2′ long and 2.5″ i.d., capped at both ends, and equipped with inlet tubes I and J and exit tube K, as well as Weston thermometer C, and elec-

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(2) E. A. Tyczkowski and L. A. Bigelow, THIS JOURNAL, **75**, 3523 (1953).

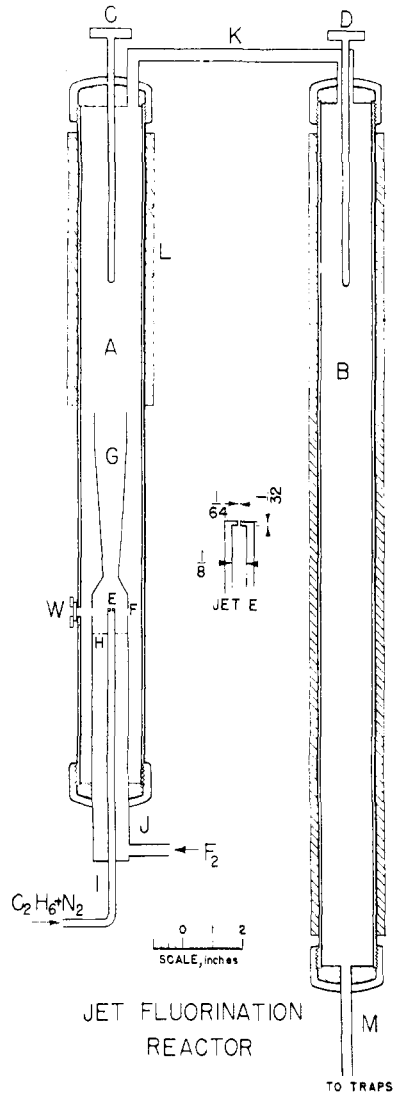

Fig. 1.

tric heater L, covering the upper part of the pipe. The large fluorine inlet J was mounted in the bottom pipe cap, and carried on its top the Venturi G, which was a Meker burner tube with the grid removed, carrying the normal gas inlets at F, which were below the jet E. The ethane inlet I passed through J and a centering device at H as indicated, and carried on its top the jet E, constructed as described in the text above and shown in the inset. Directly opposite E was a circular observation window W, 1″ in diameter, covered by a small sheet of Plexiglas held in place by a metal holder, which was in turn secured by a spring (not shown). Reactor B was an empty iron pipe, 2.5′ long and 1.75″ i.d. It was capped at both ends, electrically heated, equipped with thermometer D, inlet tube K and exit tube M.

In operation, metered ethane diluted by metered nitrogen, entered through I and the jet E, while metered fluorine came in through J and H, rising around E. The temperature at the top of the reactor was adjusted by the heater L until periodic mild explosions ceased and a steady reaction took place, accompanied by a blue glow some distance above the mouth of G. It should be noted that partially and wholly fluorinated reactor gases, necessarily relatively inert to fluorine, were continually drawn in through F and circulated, thus constituting a secondary dilution of the reactants rising through G. The mild reaction was allowed to complete itself in the moderately heated empty reactor B, and the exit gases were condensed in a series of two copper traps, the first of which was cooled by solid CO_2-acetone and the second by liquid air. The inlet and exit tubes to the second trap were tipped with 1″ sections of thin-walled stainless steel tubing to reduce heat conductivity and avoid condensation between the traps. The final products were passed over sodium fluoride to remove hydrogen fluoride and carefully rectified in the usual manner.

The performance of this unit was very satisfactory in the fluorination of ethane. At the rate of 0.08 mole C_2H_6/hr. and a molar reaction ratio of 6:1:12, corresponding to a fluorination ratio of 6:1 and a dilution ratio (N_2 in C_2H_6:F_2) of 2:1, with the temperatures at C and D both 64°, a steady state readily was obtained; and the fluorination took place largely but not wholly in the upper part of reactor A, accompanied by a quiet blue glow, centered some distance above G. The reaction was essentially completed in reactor B, and the products worked up as just described. There were obtained: CF_4 none, C_2F_6 83% of theory, forerun and residue (as C_2F_6) 11%, total recovery 94%, the C_2F_6 being 88% of the recovered product.

This new jet reactor is capable of the nearly complete conversion of C_2H_6 into C_2F_6, with an excellent recovery and very little of either cleavage or polymerization, using a continuous vapor phase process taking place in an unpacked space, both at a low dilution ratio and relatively low reactor temperature. Although this reactor has been tested as yet only under ideal conditions, there would seem to be no valid reason why its use could not be generalized, and applied successfully to the vapor phase fluorination of other volatile organic compounds.

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