CHEMICAL REACTIVITY OF CF4 AND C2F4 INDUCED BY ELECTRICAL DISCHARGE

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Electron activation in the electrical glow discharge is shown to result in extensive reaction of CF_4 with SiO_2 to CO_4 , O_2 and SiF_4 at near room temperature. Similar activation of C_2F_4 leads to liquid, mono-olefinic condensation products. The reactions are attributed to the initial formation of CF_3^+ and of $C_2F_4^+$ ions, respectively.

Introduction

In a low pressure glow discharge, because of the weak interaction of the electron and the molecular (gas) assemblies, the average energies of the two can differ by a large amount.¹ For example, in a particular case² of a discharge at 1 mm. pressure, the gas temperature was about 300°, the quasitemperature of the electron assembly, at the same time, was nearly 5000°. In such a system a steady state of electron and molecular energies can be maintained, but the distribution of chemical products need not be limited by thermodynamic equilibrium values based on the gas temperature. Furthermore, in producing electronically excited as well as ionized molecular states, the low pressure discharge may provide reaction paths unavailable in the normal thermal reaction systems.

We have studied the induction of chemical reactivity by electron activation for two perfluorocarbons: 1, pyrolysis of **tetrafluoromethane**, CF_4 , a compound of unusual thermal and thermodynamic stability^{3,4}; 2, the polymerization reaction of **tetrafluoroethylene** to liquid range olefins which is thermodynamically feasible at low temperatures but has not been successfully achieved by chemical means.

Experimental Procedure

The flow reaction system was used. The reactor consisted of one-half inch diameter Vycor tubing. An electrodeless discharge was induced by application of a radiofrequency voltage to the external electrodes. The electrodes and thus the glow discharge had a length of 3 cm. The charge gases were available at near atmospheric pressure. A needle valve determined the flow rate. The products were frozen into a trap cooled by liquid nitrogen. A valve between reactor and trap controlled the desired pressure in the reactor. A moderate pumping speed was usually maintained on the trap to eliminate the building up of noncondensable gases.

condensable gases. A controllable amount of radio-frequency power was supplied to the reactor from an oscillator amplifier. It was measured by noting the d.c. power performance of the radiofrequency amplifier and calibrating this d.c. power against the power supplied to an inductively coupled incandescent bulb. The latter was determined by the method of matching brightness between it and a second and similar incandescent bulb supplied by ordinary a.c. power through a watt meter.

Carbon tetrafluoride was obtained as a by-product from the direct fluorination of hydrocarbons and purified by low temperature fractionation. Tetrafluoroethylene was ob-

(3) O. Ruff and O. Bretschneider, Z. anorg. allgem. Chem., 210, 173 (1933).

(4) L. White, Jr., and O. K. Rice, J. Am. Chem. Soc., 69, 267 (1947).

tained from the pyrolysis of Teflon and subsequent low temperature fractionation.

Results

Carbon Tetrafluoride.—CF₄ was subjected to a cold glow discharge at a pressure of 10 mm. and a flow rate of 60 std. cc./min. Various amounts of radio-frequency power were admitted to the discharge by varying the potential across the electrodes. The glass surfaces of the reaction system remained uncoated. However, glass was etched from the reactor wall and rapid depletion of the silica wall became evident. The etching of the surface diminished to an unnoticeable amount within 0.5 cm. from the end of the gas discharge volume in the direction of gas flow. At room temperature, no visible liquid product remained in the trap. The gaseous products were analyzed by a Consolidated mass spectrometer. The analyses showed production of CO_2 , CO, SiF_4 and O_2 . The quantitative analyses are presented in Fig. 1 as a function of the electrical power input to the reactor in units of kcal. of energy input per mole of reactant. Aside from the products included in Fig. 1, traces of COF₂ and C_6F_6 at concentrations not exceeding 1% were identifiable by mass spectral analysis.

Tetrafluoroethylene.—After passing tetrafluoroethylene through the discharge reactor at pressures ranging from 40 to below 1 mm., liquid product remained in the collection trap after reaching room temperature. Production of liquids resulted in the "cold" discharge, while approach to arc discharge conditions (higher pressure, higher gas temperature) resulted in a sharp drop of liquid range products in favor of gaseous products with carbon number two and three. This is demonstrated by the results shown in Table I.

TABLE I

Performance of C₂F₄ in Flow Discharge System under Cold Discharge and near Arc Conditions

Pressure, mm.		10	40
Energy input/mole of read	ctant,		
kcal./mole	109	322	
Color of discharge		Blue	Yellow
Flow rate, std. cc./min.	62 ± 5	70 ± 10	
Liquid product yield, % of char	14	2	
Gaseous product anal.,	C_2F_4	89.7	7.4
% (fractionation	C_2F_6	1.4	61.7
and mass spectrometer)	C_3F_6	8.9	30.9

Figure 2 shows the product yield obtained *versus* energy input supplied to the reactant. These data were obtained at a flow rate of 50 std. cc./min. by varying the electrical power to the reactor by varia-

⁽¹⁾ A. V. Engel and M. Steenbeck, "Elektrische Gasentladungen," Vol. I, Julius Springer, Berlin, 1932, p. 53.

⁽²⁾ C. G. Found, *I.E.S. Trans.*, **33**, 161 (1938); J. D. Cobine, "Gaseous Conductors," McGraw-Hill Book Co., New York, N. Y., 1941, Chapter 9.

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Cut label	"Pot" temp., °C.	Wt., g.	Total wt. distilled, g.	В. р., °С.	n ²⁰ D	NF - NC Read.	Remarks	
в	70-80	0.0716	0.0716	Below R.T.	1.280	0.06055		
С	80-100	.1638	.2354	Below R.T.	1.280	. 06055		
D	100-140	.1252	.3606	32	1.285	.05537		
\mathbf{E}	140 - 195	.1367	.4973	72.2-73.3	1.293	.05611		
G	195 - 250	.0549	.5522	?	1.298	.05632		
I	120	.1176	.6698	140 - 145	1.3250	.05524	At $p = 1$ mm.	
\mathbf{S}	120 - 200	.0222	.6920	165 - 180	1.3427	.05469	At $p = 1$ mm.	

TABLE II

PROPERTIES OF LIQUID REACTION PRODUCTS FROM C₂F₄ REACTION, OBTAINED BY MICRODISTILLATION

tion of the electrode potential at two constant pressures, 0.2 and 1 mm. The reactor in this experiment consisted of two concentrical cylindrical Pyrex tubes, 35 mm. and 87 mm. diameter, 175 mm. long.



Fig. 1.— CF_4 reaction product concentration for various amount of energy supplied to the reactor per unit quantity of reactant in kcal./mole and in ev. molecule.

In contrast to the case of carbon tetrafluoride, no detectable reaction with silica occurred. Elemental analyses showed the liquid products to be perfluorocarbons of C_6 average carbon number.



Fig. 2.—Weight percentage of C_2F_4 converted to liquid product for various amounts of energy supplied to the reactor per unit quantity of reactant.

A micro-distillation⁵ on a Craig⁶ column of ten theoretical plates on 1.5681 g. of liquid product resulted in the data summarized in Table II. It is possible to obtain a semi-quantitative picture of unsaturation by comparing boiling points and re-

(5) The author is indebted to I. A. Breger, Geology Dept., M.I.T., and his assistants for their indispensable help in obtaining these microdistillation data.

(6) L. C. Craig, Ind. Eng. Chem., Anal. Ed., 9, 441 (1937).

fractive indices of the individual cuts from the micro-distillation with those of known compounds. This comparison is undertaken in Fig. 3. In the



Fig. 3.—Deduction of degree of unsaturation of liquid products obtained from C_2F_4 , by comparing boiling points and refractive indices with those of known compounds. ||||, known compounds; ////, properties of distillation cuts; D. B., double bonds.

upper portion, boiling points of four of the distillation cuts are used to derive their carbon number by comparison with known compounds. In the lower portion of the graph this information is combined with the values of the refractive index of the respective cuts. It will be seen that unsaturation of about one double bond per molecule is indicated. This mono-olefin character of the product was further confirmed by the nature of the mass spectrometer patterns and later by chlorination.

Discussion and Conclusions

Carbon Tetrafluoride.—The product analyses shown in Fig. 1 show that CF_4 reacted with SiO_2

at up to 60% conversion during a molecular residence time of about 0.06 second in the discharge space at a temperature $\sim 100^{\circ}$. The over-all reaction can be described well by the formula

$$5CF_4 + 5SiO_2 \longrightarrow 3CO_2 + 2CO + 1O_2 + 5SiF_4$$

The analytical deficiency in SiF₄ is well explained
by contact with traces of water previously observed
in mass spectrometer analyses.

Mass spectrometer studies' show that the ionization process of the parent molecule, *i.e.*, $CF_4 \rightarrow CF_4^+ + e^-$, does not occur. The first ion producing mechanism occurring at lowest electron energy (15.9 e.v.) yields CF_3^+ ions. Since an electrical discharge is produced only by virtue of an electron multiplication process accompanying molecular ionization, it follows a priori that chemical dissociation will necessarily accompany the occurrence of a discharge in CF_4 . There is evidence,' furthermore, that the production of CF_3^+ ion does not generate an electron but occurs as $CF_4 \rightarrow CF_3^+ + F^-$. The first electron producing ionization process may be the reaction

 $CF_4 \longrightarrow CF_3^{++} + F^- + e^-$

requiring 43.8 e.v. electron energy, which would necessarily be the initial process of consumption of CF_4 molecules. The results in Fig. 1 show that

(7) V. H. Dibeler and F. L. Mohler, J. Research Natl. Bur. Standards, 40, 25 (1948).

an appreciable fraction of CF_4 is indeed converted when the average electrical energy per molecule exceeds some 40 e.v., which supports the view that the initiating process is the highly energetic step indicated above.

Tetrafluoroethylene.—The cold electrical discharge successfully induces condensation reactions of C_2F_4 leading to liquid mono-olefins.

In case of C_2F_4 the production of the parent ion $C_2F_4^+$ is known to be the energetically lowest ion and electron producing process at 10.3 e.v. It must be held responsible for the sustenance of the glow discharge and for yielding $C_2F_4^+$ as the initial active species resulting in further chemical reaction. This view finds support in the observation of Fig. 3 that a large fraction of tetrafluoroethylene undergoes chemical conversion to products of three times the original molecular weight when the average energy supplied is as low as $10.3/3 \approx 3$ e.v. Absence of any reaction with SiO₂ speaks further for the absence of fragment ion production which would split off F or F₂.

Ion neutralization in collision with the wall is a highly exothermic process accompanied by dissociation⁸ which can easily give rise to product molecules of odd carbon numbers, as are seen in the gas analysis shown in Table I.

(8) P. B. Weisz, This Journal, 52, 578 (1948).

THE ELECTRICAL CONDUCTANCE OF WEAK ACIDS IN ANHYDROUS HYDRAZINE¹

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The conductance of dilute solutions of phenol and four substituted phenols in hydrazine has been measured at 25°. Dissociation constants varying from 1.8×10^{-4} for *p*-cresol to 6.4×10^{-3} for *p*-chlorophenol were obtained. Conductance in the water-hydrazine system over the complete composition range was measured. For dilute aqueous solution a dissociation constant for hydrazine as a base of 9×10^{-7} was calculated. Water in nearly anhydrous hydrazine was found to be an extremely weak electrolyte.

Anhydrous hydrazine, having a liquid range similar to that of water, has a relatively high dielectric constant, 51.7 at 25°, according to Ulich and Nespital,³ and is known to be a good solvent for many salts. As it has not been employed as a solvent to any great extent, presumably because of its instability and rapid contamination when exposed to the atmosphere, it seemed worthwhile to investigate further its behavior as a solvent for electrolytes. Walden and Hilgert⁴ prepared anhydrous hydrazine having a specific conductance of 2–3 $\times 10^{-6}$ ohm⁻¹ cm.⁻¹ and measured the conductance of a number of electrolytes in this solvent. These investigators found that salts in hydrazine, with due allowance for the difference in dielectric constant, behaved much like they do in water. The strongly basic nature of the solvent, however, promoted such acids as benzoic, of $K = 6 \times 10^{-5}$ in water, to strong electrolytes in hydrazine.

For the present investigation, it was decided to study such weak acids that, even in hydrazine, dissociation would be incomplete, so that the change in dissociation constant accompanying the change in medium could be measured. For this purpose, phenol and four substituted phenols were selected. In addition, the conductance of water-hydrazine mixtures was measured over the complete range of composition, and the conductance of methyl alcohol in hydrazine was measured. Dissociation constants for the phenols in hydrazine have been evaluated, but the conductance of water and methyl alcohol was found to be too small for quantitative treatment. The conductance of dilute solutions of hydrazine in water was measured and its ionization constant calculated for comparison with previously reported values.

⁽¹⁾ This research was supported by the United States Air Force under contract No. AF(600)-448 monitored by the Office of Scientific Research.

⁽²⁾ From the Ph.D. thesis of Leon J. Vieland, June, 1954.

⁽³⁾ H. Ulich and W. Nespital, Z. physik. Chem., B16, 221 (1932).

⁽⁴⁾ P. Walden and H. Hilgert, *ibid.*, **A165**, 241 (1933).