trogen flow adjusted to give isothermal conditions at a steady state. This meant that the energy balance was obtained only at the end of the run. While this energy balance was being taken, the chlorine was directed to the potassium hydroxide tower and a sample collected at the same flow rate as used in the reaction. The amount of chlorine in the sample was determined as described previously.

The products resulting while the calorimeter was at a steady state were condensed in a trap at −80°. Infrared absorption spectra[18] were taken on the first, middle and last fraction of the sample. By comparing the curves so obtained with those given by the pure olefin and dichloride, it was shown that no appreciable amounts of disproportionation or degradation reactions took place on the catalyst. The curves for the pure materials are given in Figs. 3a and 3b.

The data obtained on the chlorination of tetrafluoroethylene are summarized in Table IV. The results are quite reproducible and show that the heat of chlorination of this olefin is considerably greater than that of ethylene which is 43,600 calories.[3]

TABLE IV

HEAT OF CHLORINATION OF TETRAFLUOROETHYLENE AT 90°

Run no.	Olefin flow, moles/min. $\times 10^{+4}$	Chlorine flow, moles/min. $\times 10^{4}$	Energy rate, cal./min.	$-\Delta H$, cal./mole
29	7.60	5.101	29.22	57,283
30[a]	8.25	5.77	33.04	57,262
31	9.04	6.071	34.86	57,420
32	6.93	6.109	35.02	57,325

[a] The chlorine flow was read off the flow meter in this case rather than being determined by direct analysis.

Acknowledgment.—This work was made possible by a grant from the Research Corporation of New York. A special grant from the Regents of the University of Colorado made possible the purchasing of the infrared spectrometer. We wish to thank Mr. C. Walden and K. Lea for assistance in operating the calorimeter and infrared spectrometer. Mr. D. K. Vail assisted in the preparation of some of the compounds used and Mrs. C. M. Snow carried out the analysis for chlorine. Mr. E. Holderby constructed the calorimeter proper and most of the accessories in the shops of the University of Colorado.

Summary

An isothermal constant-flow calorimeter is described which is suitable for measuring heats of vapor phase reactions at temperatures up to 90°. By measuring the heat of hydrogenation of cyclohexene and the heat of formation of hydrogen chloride and comparing the results obtained with data existing in the literature, the calorimeter was shown to give heats of reactions to an accuracy of one per cent. The vapor phase heat of chlorination of tetrafluoroethylene was measured to be $\Delta H = -57{,}322 \pm 200$ calories per mole at 90°.

BOULDER, COLORADO RECEIVED OCTOBER 25, 1948

---

[18] The instrument is a model 12B manufactured by the Perkin-Elmer Corporation of Glennbrook, Conn.

[CONTRIBUTION FROM THE UNIVERSITY OF COLORADO]

Reaction Heats of Organic Fluorine Compounds. II. The Vapor Phase Heats of Chlorination of Some Simple Fluoroölefins[1,2]

BY J. R. LACHER, J. J. MCKINLEY, C. WALDEN, K. LEA AND J. D. PARK

In the first paper of this series[2] an isothermal constant flow calorimeter was described. The performance of the equipment was determined by measuring the heat of hydrogenation of cyclohexene and the heat of formation of gaseous hydrogen chloride. New data on the vapor phase chlorination of tetrafluoroethylene were also presented. The present paper deals with the vapor phase heats of chlorination of trifluorochloroethylene, 1,1-dichloro-2,2-difluoroethylene, perfluoropropene and perfluorocyclobutene.

Preparation of Compounds.—The trifluorochloroethylene[3] was purified by a low temperature distillation in a vacuum-jacketed column packed with glass helices using a magnetic take-off head and a reflux ratio greater than 5 to 1. The still head was cooled by circulating a carbon tetrachloride–chloroform–Dry Ice mixture from a reservoir at such a rate as to maintain about a 20° differential between the still head and the boiling point of the olefin. A forecut was discarded and the center fraction having a boiling point variation of less than 0.1° was collected and stored in a steel cylinder for subsequent use. The infrared absorption spectrum is shown in Fig. 1a. Using auxiliary equipment, a sample of the chlorine adduct of trifluorochloroethylene was prepared. A flow system identical with that used in the calorimeter was employed and the chlorination was carried out in the presence of ferric chloride–impregnated carbon catalyst previously described. After distillation, the product, 1,1,2-trifluoro-1,2,2-trichloroethane, gave an absorption spectrum as shown in Fig. 1b. The isomer of this compound,[3] 1,1,1-trifluoro-2,2,2-trichloroethane, gives an absorption spectrum as shown in Fig. 1c. By studying the spectrum of the product formed in an actual calorimetric run, it was concluded that little or no disproportionation occurred on the catalyst. However, if the olefin was not pure, the absorption spectrum of the calorimeter product was not a combination of those shown in Figs. 1a and 1b. Instead, anomalous absorption peaks appeared at 6.50 and 11.77 μ, hydrochloric acid was in the effluent gases and the heat of reaction was low. The trouble was overcome by scrubbing the olefin in the purification train described in Paper I of this series.[2] The 1,1-dichloro-2,2-difluoroethylene and perfluoropropene[3] were passed through the purification train and then sent directly to the calorimeter. The infrared absorption spectra of 1,1-dichloro-2,2-difluoroethylene and its chlorine adduct, 1,1,1,2-tetrachloro-2,2-

---

[1] Presented before the Division of Inorganic and Physical Chemistry, 114th Meeting of the American Chemical Society, Portland, Oregon, September 13-17, 1948.

[2] J. R. Lacher, J. J. McKinley, C. M. Snow, L. Michel, G. Nelson and J. D. Park, THIS JOURNAL, **71**, 1330 (1949).

[3] A generous sample was supplied us through the couretsy of the Jackson Laboratory, du Pont Co., Wilmington, Delaware.

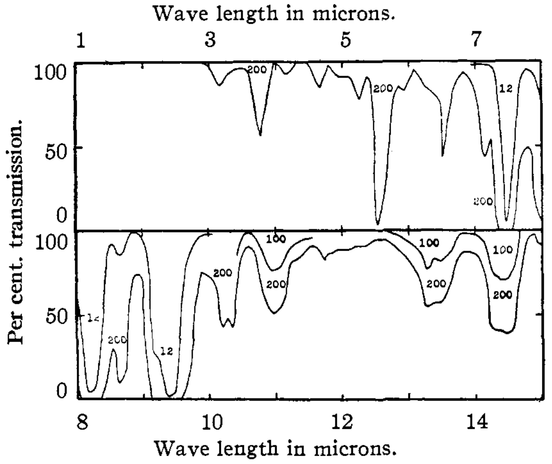


Fig. 1A.—Infrared absorption spectrogram of CF_2=CFCl gas at room temperature in 10-cm. cell at ind. mm. pressure.

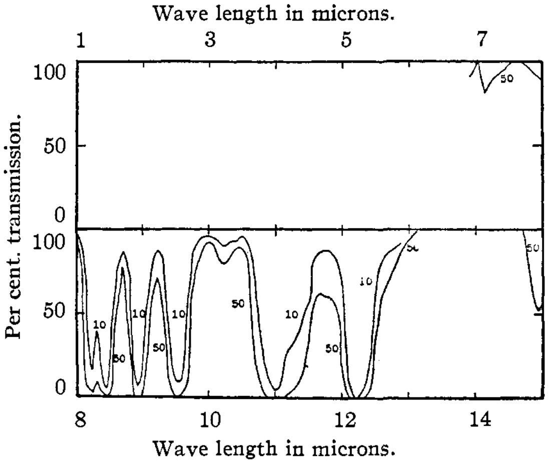


Fig. 1B.—Infrared absorption spectrogram of CF_2Cl—$CFCl_2$ gas at room temperature in 10-cm. cell at ind. mm. pressure.

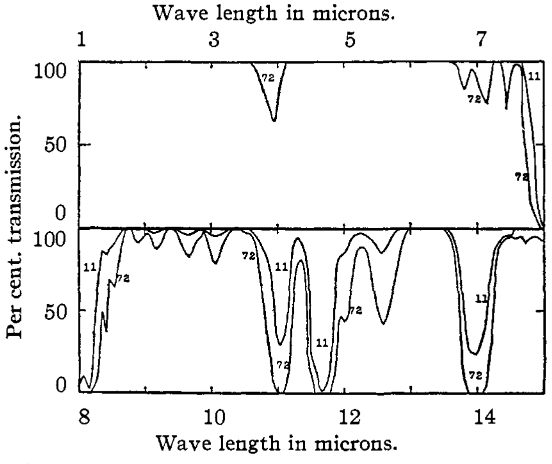


Fig. 1C.—Infrared absorption spectrogram of CF_3—CCl_3 gas at room temperature in 10-cm. cell and ind. mm. pressure.

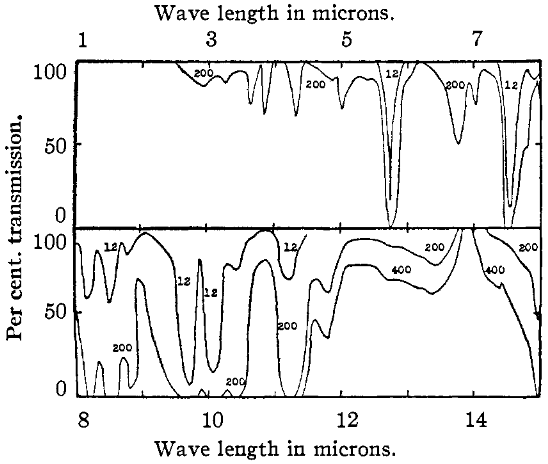
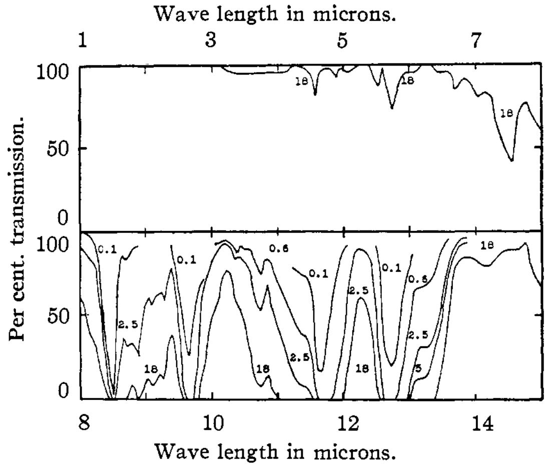


Fig. 2A.—Infrared absorption spectrogram of CF_2=CCl_2 gas at room temperature in 10-cm. cell and ind. mm. pressure.



Fib. 2B.—Infrared absorption spectrogram of CF_2Cl—CCl_3 gas at room temperature in 1-meter cell and ind. mm. pressure.

difluoroethane, are given in Figs. 2a and 2b, respectively. The absorption spectra of perfluoropropene and its chlorine adduct are given in Figs. 3a and 3b, respectively.

The perfluorocyclobutene was prepared[4] by dimerization of trifluorochloroethylene followed by subsequent removal of two chlorine atoms by alcoholic zinc.[5] The olefin was purified by distillation in a modified Podbielniak column packed with glass helices using a reflux ratio of about 15 to 1. The forecut was discarded and the center cut, having a boiling point constant to 0.1°, was collected and stored in a steel cylinder for subsequent use. The olefin was also sent through the scrubbing train before entering the calorimeter. The infrared absorption spectrum is shown in Fig. 4a. The absorption spectrum and freezing point of the chlorine adduct depend on how the material is prepared.[6] The absorption spectrum of the compound produced by catalytic chlorination at 90° is shown in Fig. 4b and is probably a mixture of *cis-trans* isomers.

---

(4) We wish to thank Dr. M. L. Sharrah of this Laboratory for the preparation of this compound.

(5) A. L. Henne and W. J. Zimmerschied, THIS JOURNAL, **69**, 281 (1947).

(6) Unpublished work of this Laboratory.

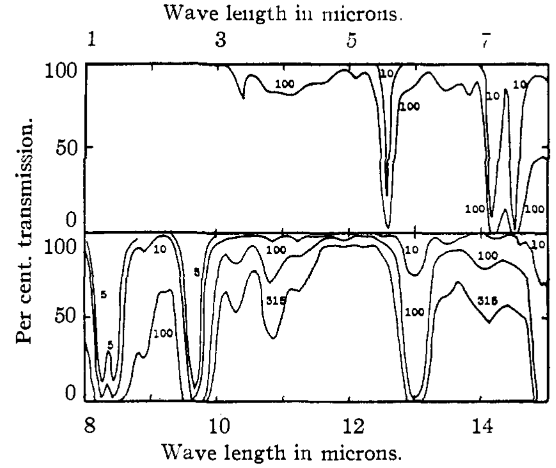


Fig. 3A.—Infrared absorption spectrogram of CF_3—CF=CF_2 gas at room temperature in 10-cm. cell and ind. mm. pressure.

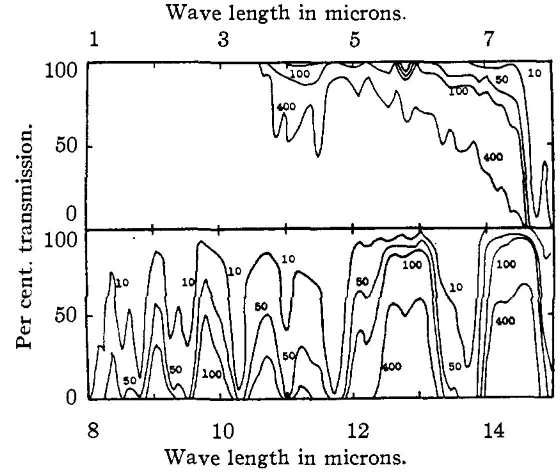


Fig. 3B.—Infrared absorption spectrogram of CF_3—$CFCl$—CF_2Cl gas in 10-cm. cell and ind. mm. pressure.

Experimental Results.—The procedure used in making a run was similar to that described in Paper I[2] for the chlorination of tetrafluoroethylene. The chlorine was mixed in the catalyst chamber with an excess of olefin. The product gases were tested for unreacted chlorine and the presence of hydrogen chloride. They were found to be absent. In the case of trifluorochloroethylene some difficulty was experienced in obtaining products free of hydrogen chloride and with perfluorocyclobutene a high olefin to chlorine ratio was necessary to ensure complete reaction.

New reagents were used in the scrubbing train whenever the olefin was changed; a new catalyst, however, was not always used. The products of a previous run were thoroughly removed by displacement with dry nitrogen until no organic fluorine compounds could be detected in the effluent. The catalyst chamber was then evacuated for several hours and the system then filled with nitrogen.

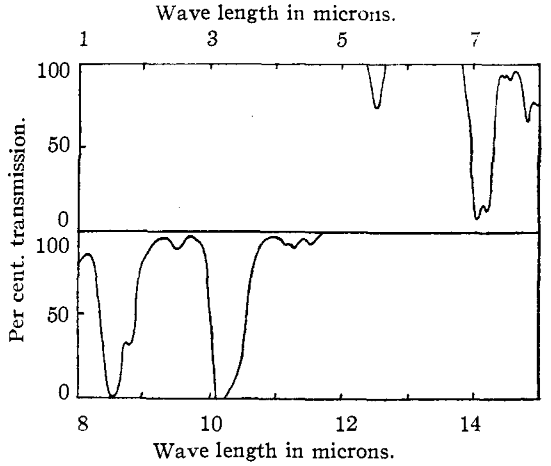


Fig. 4A.—Infrared absorption spectrogram of CF_2—CF=CF—CF_2 gas at 10 mm. pressure, room temperature and in 10-cm. cell.

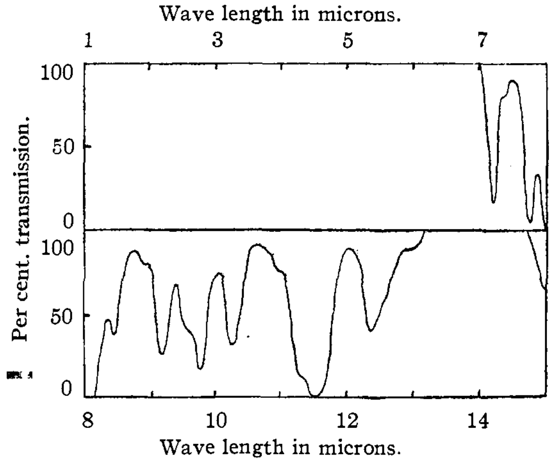


Fig. 4B.—Infrared absorption spectrogram of CF_2—$CFCl$—$CFCl$—CF_2 gas at 11 mm. pressure, in 10-cm. cell at room temperature, thermal chlorination.

After the catalyst had reached a steady state, the products were collected for thirty minutes or more in a Dry Ice-trap and reserved for infrared analysis. Two separate series of infrared spectra were obtained from each of the runs. The first was obtained by drawing off at −80° a vapor sample into the absorption cell. This sample was run at several pressures necessary to obtain absorption peaks. This foreshot was rich in olefin and should have contained the low boiling impurities, if present. The second series of spectra were run after distilling off most of the olefin and then taking a sample. This tail fraction consisted mainly of the chlorine adduct and should have any high boiling impurities, if present. The analysis was again carried out at several pressures. Slight amounts of impurities would be detected at the higher pressure runs and the low pressure analysis served to identify the olefin and chlorine adduct. A comparison of the spectra so obtained with those shown by the purified olefin and chlorine adduct showed the presence of no new bands. Since some of the bands given by fluorocarbons are very intense, we believe that any undesirable side reactions, if they took place at all, were less than 0.2%.

The results obtained on chlorinating the four olefins at 90° are summarized in Table I. All of the experiments are reported except in the case of trifluorochloroethylene. Many experiments using this compound served merely in developing the technique of handling the calorimeter, purification method for the olefin and the method of analysis for the chlorine sample. In this case only the last three runs are included. It is believed that the average values for the vapor phase heats of chlorination are reliable to about 1%.

TABLE I

VAPOR PHASE HEATS OF CHLORINATION AT 90°

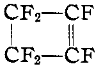
Run	Olefin flow, moles/min. × 10⁴	Cl_2 flow, moles/min. × 10⁴	Energy input, cal./min.	$-\Delta H_{363}$ °K. cal./mole
		Trifluorochloroethylene		
43	8.6	5.8616	28.759	49,063
44	8.9	6.3200	30.993	49,040
45	8.9	6.4346	31.106	48,342
		Average 48,815 ± 475 cal./mole		
		1,1-Dichloro-2,2-difluoroethylene		
39	6.2	5.2633	21.628	41,092
40	6.2	5.4325	22.725	41,832
41	6.2	5.9512	24.114	40,520
42	6.5	6.1930	25.306	40,862
		Average 41,076 ± 556 cal./mole		
		Perfluoropropene		
46	6.7	4.8014	22.635	47,142
47	6.4	5.0244	23.636	47,042
48	8.0	5.9983	23.624	47,264
		Average 47,149 ± 115 cal./mole		
		Perfluorocyclobutene		
50	6.8	2.2709	8.6209	37,962
51	9.6	2.9701	11.134	37,487
52	5.7	2.6600	10.020	37,669
53	5.7	3.4052	12.390	36,386
		Average 37,376 ± 990 cal./mole		

Discussion of Results

The vapor phase heats of chlorination obtained to date are summarized in Table II. Also included in the table is the heat of chlorination of ethylene as determined by Kistiakowsky and coworkers.[7] It is apparent that for this series of reactions there are strong deviations from the additivity rule. The heat of chlorination of tetrafluoroethylene is 20 kcal. greater than that of perfluorocyclobutene. When one fluorine in tetrafluoroethylene is replaced by chlorine, the reaction heat drops 8.5 kcal. When two are replaced on the same carbon, the heat drops by 16.2 kcal. or just twice. If the fluorine in tetrafluoroethylene is replaced by a CF_3-group, the heat drops by 10.1 kcal. and the CF_3- group has a greater effect than a chlorine atom. In this case, one of the added chlorine atoms is on a carbon containing a CF_3-group and a fluorine atom and is, therefore, "secondary." When chlorine adds to perfluorocyclobutene, both the chlorine atoms go into secondary positions. The lowering of the heat is 19.9 kcal. or just twice that shown by perfluoropropene. Systematic generalizations concerning the deviations from the additivity rule will, of course, have to wait upon further experimentation.

TABLE II

VAPOR PHASE HEATS OF CHLORINATION

Compound	$-\Delta H_{363}$, cal./mole
$CF_2{=}CF_2$	57,323
$CF_2{=}CFCl$	48,815
$CF_2{=}CCl_2$	41,076
$CF_2{=}CF{-}CF_3$	47,149
	37,376
$CH_2{=}CH_2$[a]	43,600

[a] Reference 7.

The calorimetric studies of Swarts[8] show that rather large deviations from the additivity rule are to be expected. For the series ethyl alcohol, monofluoroethanol and difluoroethanol, his data show that 9 kcal. more heat is liberated when a second hydrogen is replaced by fluorine than obtains for the first one. The difference in stability of the -CHF- and -CF_2- groups is accounted for by thermochemical data. The same is true for the reactions studied here.

Acknowledgment.—This work was made possible by a grant from the Research Corporation of New York.

Summary

The vapor phase heats of chlorination of trifluorochloroethylene, 1,1-dichloro-2,2-difluoroethylene, perfluoropropene and perfluorocyclobutene have been measured at 90°. The heats of these reactions deviate strongly from the additivity rule.

BOULDER, COLORADO RECEIVED OCTOBER 25, 1948

---

[7] J. D. Conn., G. B. Kistiakowsky and E. Smith, THIS JOURNAL, **60**, 2764 (1938).

[8] E. Swarts, *J. chim. phys.*, **17**, 3 (1919).