suggest that this method of estimating ring-chain entropies may be useful in many cases where a complete statistical thermodynamic calculation is impractical. Acknowledgment.—We would like to thank Professor R. C. Minnick for his valuable advice on computing procedures, and for making available to us the necessary computer time.

# NOTES

## REACTION HEATS OF ORGANIC HALOGEN COMPOUNDS. VI. THE CATALYTIC HYDROGENATION OF SOME ALKYL FLUORIDES<sup>1</sup>

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In a previous paper<sup>2</sup> an isothermal constant flow calorimeter was described which operated at a temperature of about 248°. Its reliability was determined by measuring the heat of formation of HCl; we also reported the heats of hydrogenation of methyl, ethyl and vinyl chlorides. The present paper deals with the catalytic hydrogenation of methyl, ethyl, *n*-propyl and isopropyl fluorides. Only the last two reactions were sufficiently quantitative to permit calorimetric measurements.



Fig. 1.—Infrared spectra of (A) normal propyl fluoride; (B) isopropyl fluoride; gas at room temp. in 10-cm. cell at indicated mm. pressure; Perkin-Elmer single beam spectrometer with sodium chloride optics.

**Experimental Details.**—Methyl and ethyl fluorides<sup>3</sup> were prepared by the reaction of the corresponding iodides with mercuric fluoride. The apparatus consisted of a oneliter copper reaction flask equipped with a copper condenser

(1) This research was supported by the A.E.C. Contract No. AT (29-1), Program A.

(2) J. R. Lacher, E. Emery, E. Bohmfalk and J. D. Park, THIS JOURNAL, **60**, 492 (1956).

(3) A. L. Henne and Thomas Midgley, Jr., J. Am. Chem. Soc., 58, 884 (1936).

and an inlet for the mercuric fluoride. The methyl fluoride was purified by a simple trap to trap distillation. The ethyl fluoride was purified by distilling in a low temperature Podbielniak column. It boiled at  $-46^{\circ}$  at 625 mm. Five hundred grams of *n*- and isopropyl fluorides were prepared using a procedure described by Grosse and Linn.<sup>4</sup> The compounds were carefully purified by distilling in a 100plate Podbielniak column. The *n*-propyl fluoride boiled at -9.0 to  $-8.8^{\circ}$  and the isopropyl at  $-15.6^{\circ}$  at a pressure of 627.7 mm. mercury. The infrared spectra of the compounds in the region between 2 and  $15\mu$  are illustrated in Fig. 1. A sodium chloride prism and optics were used in this determination.

The catalyst used consisted of palladium on activated carbon. The carbon was sized so that it passed a 6 and was retained by a 20 mesh screen. It was first treated with 10% nitric acid, washed several times with distilled water, dried at 100°, and finally evacuated for 24 hours at 350° and about 1 mm. pressure. Eight grams of palladium chloride was dissolved in 50 ml. of 15% hydrochloric acid and the solution was added to 65 g. of purified activated carbon. The mixture was dried over a steam-bath and placed in a catalyst chamber. Hydrogen was passed through at a temperature of 248° to reduce the palladium chloride. After the reduction was complete, the catalyst was evacuated at 1 mm. for 24 hours.

In order to determine the effectiveness of the catalyst in bringing about the hydrogenation of the alkyl fluorides in question, the reactions were studied in a pilot plant. The flow rates of the hydrogen and organic material were set to be approximately those to be used in a calorimetric measurement. The catalyst chamber was placed in an electrically heated can for convenient though approximate temperature control. The exit gases were passed through a tube containing sodium fluoride pellets to remove hydrogen fluoride. The products were analyzed by means of infrared absorption. The strong band at  $10.30\mu$  shown by *n*-propyl fluoride (Fig. 1) and that at  $12.25\mu$  in isopropyl fluoride occur in regions where propane is transparent. The intensities of these peaks were measured at different pressures and used as reference for quantitative analyses.

Therefore for quantitative analyses. Using a flow rate for hydrogen of  $1.0 \times 10^{-3}$  mole/min. and for isopropyl fluoride  $0.5 \times 10^{-3}$  mole/min., it was found that the reaction was quantitative at the temperatures of 235, 200 and 155°. At 110° only about 5 to 10% conversion was obtained. Using the same flow rates it was found that *n*-propyl fluoride was more difficult to hydrogenate. If a new and active catalyst was used, the reaction was quantitative at temperatures of 190° and above. Even though elaborate precautions were taken, the maximum conversion of methyl and ethyl fluoride to methane and ethane was 10% at 240°. In making a calorimetric run hydrogen was used in

In making a calorimetric run hydrogen was used in excess. The rate of reaction was taken as being equal to the rate of formation of hydrogen fluoride. The reaction products were diverted for a known length of time to a copper collecting tower filled with Teflon chips. The absorbing solution consisted of 100 ml. of dilute sodium hydroxide. The excess hydroxide was titrated with a standard 0.05 N sulfuric acid solution. Of eight runs made on *n*-propyl fluoride, seven were completed without experimental difficulties and are given in Table I.

Discussion of Results.—In order to use the present results to calculate the standard heats of

(4) A. V. Grosse and C. B. Linn, J. Org. Chem., 3, 26 (1938).

#### TABLE I

HYDROGENATION OF n-PROPYL FLUORIDE, 248°

TT	HF	<b>D</b>	
H <sub>2</sub> now,	formation,	Energy	$-\Delta H$
moles/min.	moles/min.	rate,	real./mole
X 104	$\times 10^{4}$	cal./min.	$n-C_{s}H_{7}F$
6.20	3.050	6.887	22.58
8 50	9 490	5 477	00 62
0.00	4.440	0,417	22.00
6.55	3.000	6.807	22.69
8.45	4 025	9 353	22 24
	1,010	0.000	
8.30	4.025	9.244	22.97
8.30	3,000	6.942	23, 14
7 00	3 015	6 023	22 06
1,00	0.010	0.040	22.00

 $-\Delta H$  av. 22.88 kcal./mole Twice the stand. dev. from the mean:  $\pm 1.6\%$ 

Five runs were made on isopropyl fluoride and they are given in Table II.

Table II

Hydrogenation of Isopropyl Fluoride, 248°

H2 flow moles/min. × 104	$\begin{array}{c} \text{HF} \\ \text{formation,} \\ \text{moles/min.} \\ \times 10^4 \end{array}$	Energy rate, cal./min.	$-\Delta H$ , kcal./mole iso-CaH7F
7.00	3.215	6.692	20.85
8.00	4.52	9.563	21.16
7.30	3.50	7.419	21.19
7.45	3.50	7.445	21.27
7.45	3.013	6.346	21.06

 $<sup>-\</sup>Delta H$  av. 21.11 kcal./mole

Twice the stand. dev. from the mean:  $\pm 0.69\%$ 

formation of *n*- and isopropyl fluoride, it is necessary to know their gaseous heat capacities in the range between 25 and 248°. The data are not available. However, it is possible to calculate the heat of isomerization of normal to isopropyl fluoride at 248°. One finds that the iso compound is more stable by 1.80 kcal./mole. The uncertainty in this value is about 2%.

### THE NATURE OF THE ACTIVATED INTER-MEDIATE IN THE HOMOGENEOUS CATA-LYTIC ACTIVATION OF HYDROGEN BY CUPRIC SALTS

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In an earlier paper,<sup>1</sup> a kinetic study of the Cu<sup>++</sup>catalyzed reduction of  $Cr_2O_7^{=}$  and other substrates by  $H_2$ , was described. At low acidities, the kinetics were found to be of the form

$$-d[H_2]/dt = k[Cu^{++}][H_2]$$
(1)

suggesting that an  $H_2$  molecule reacts homogeneously with a Cu<sup>++</sup> ion in the rate-determining step, leading to the formation of an "activated intermediate" which reduces  $Cr_2O_7$ — in a subsequent fast reaction.

It was reported<sup>1</sup> that the rate of this reaction decreased slightly as the concentration of  $HClO_4$  was increased, but the limitations of the equipment which was available at that time, precluded any studies with solutions containing more than 0.1 M $HClO_4$ . However, by using a titanium-lined auto-

(1) E. Peters and J. Halpern, THIS JOURNAL, 59, 793 (1955).

clave, we have since been able to extend the investigation to solutions of higher acidity. The results of this work are reported here since they throw some further light on the mechanism of the reaction and on the nature of the activated intermediate which is formed in the rate-determining step.

The procedure was the same as that employed earlier,<sup>1</sup> *i.e.*, the rate of reaction of H<sub>2</sub> was calculated from the measured zero-order rate of reduction of  $Cr_2O_7$ - using the known stoichiometry of the reaction, *i.e.* 

$$\operatorname{Cr}_{2}\operatorname{O}_{7}^{-} + 3\operatorname{H}_{2} + 8\operatorname{H}^{+} \longrightarrow 2\operatorname{Cr}^{+++} + 7\operatorname{H}_{2}\operatorname{O}$$
(1)

The decrease in rate as the  $HClO_4$  concentration was increased is shown in Fig. 1. At 1 *M*  $HClO_4$  the rate was only about 30% of its value at low  $HClO_4$ concentrations.



Fig. 1.—Dependence of the rate of reaction of  $H_2$  on the  $H^+$  concentration at 0.1 *M* Cu<sup>++</sup>, 110°, 20 atm.  $H_2$ : O, rate vs.  $[H^+]$ ;  $\Box$ , rate<sup>-1</sup> vs.  $[H^+]$ .

An earlier suggestion<sup>1</sup> that this apparent decrease in rate might be due to the reduction of  $ClO_4^-$  competing with that of  $Cr_2O_7^-$  appears untenable in the light of our failure to detect any  $Cl^-$  in the solutions and of our observations that the rate depends only on the concentration of H<sup>+</sup> and is insensitive to variations in the  $ClO_4^-$  concentration.

An alternative interpretation is that the rate-determining step, in which  $H_2$  is converted to a reactive intermediate complex, releases an  $H^+$  ion and that the decrease in rate is due to the fact that the reversal of this step, which regenerates  $H_2$ , competes with the subsequent reaction of this complex, *i.e.*, with the reduction of  $Cr_2O_7^-$ . The zero-order dependence of the rate on the  $Cr_2O_7^-$  concentration, even at high  $H^+$  concentrations, suggests that the complex does not react directly with  $Cr_2O_7^-$ . The most likely alternative is that it reacts with another  $Cu^{++}$  ion, reducing it to  $Cu^+$ , which in turn reacts rapidly with  $Cr_2O_7^-$ . These steps are incorporated in the mechanism