

sensitized reaction in solution and probably for photosynthesis *in vivo*, it is possible to rule out one mode of action: primary oxidation of the chlorophyll by the oxidant, followed by its reformation by the reductant.

Acknowledgments.—We are deeply indebted to Professor A. H. Brown of the Department of Botany for permission to use his combustion train and sample bulbs, and to Mr. J. M. Daly for running about one third of the combustions and help-

ing in other ways. We also wish to thank Professor B. L. Crawford of this Department for the use of his infrared spectrophotometer. This instrument was operated by Messrs. B. Zaslów and W. Schwabacher. Professor A. O. Nier's mass spectrometer was operated by Dr. R. Halsted and Mr. T. Griffith. We also acknowledge valuable discussions with Professors B. L. Crawford, A. H. Brown and A. W. Frenkel.

MINNEAPOLIS, MINNESOTA

[SUN OIL COMPANY RESEARCH LABORATORY]

Reactions of Hydrocarbons Induced by Alkyl Fluoride Boron Trifluoride. IV. Stoichiometry of the Self-alkylation of Isobutane

BY CONARD K. DONNELL AND ROBERT M. KENNEDY

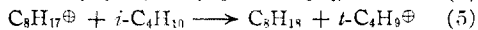
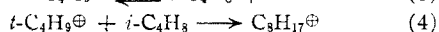
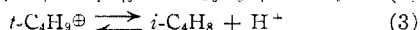
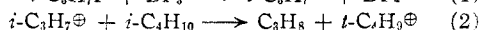
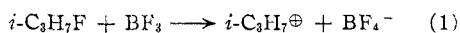
RECEIVED JANUARY 10, 1952

The self-alkylation of isobutane at -80° , as promoted by isopropyl fluoride and boron trifluoride, has been quantitatively investigated. The equation is: $\text{BF}_3 + 2i\text{-C}_3\text{H}_7\text{F} + 4i\text{-C}_4\text{H}_{10} \xrightarrow{-80^\circ} 2\text{C}_8\text{H}_{18} + 2\text{C}_3\text{H}_8 + \text{BF}_3 \cdot 2\text{HF}$. More than 0.5 mole of boron trifluoride per mole of isopropyl fluoride produces no additional reaction. The octanes produced are principally 2,2,4-trimethylpentane plus other trimethylpentanes. Very small amounts of hydrocarbons other than octanes are formed. A possible explanation of the observed stoichiometry is given.

Introduction

Under the influence of an alkyl fluoride and boron trifluoride, isoparaffins undergo a self-alkylation reaction in which two or more molecules of isoparaffin unite to form a higher molecular weight saturated hydrocarbon.¹ The experiments described here were performed to study the reaction quantitatively and to elucidate some points concerning the mechanism of the reaction. In order to eliminate side reactions, these experiments were performed at -80° . The particular reactants chosen were boron trifluoride, isopropyl fluoride and isobutane.

The sequence of reactions which occurs is believed to be^{1,2}



i-Propyl fluoride was chosen for this investigation rather than *t*-butyl fluoride so that it would be possible to distinguish the paraffin formed in equation 2 by saturation of the carbonium ion from the original isobutane charged. If *t*-butyl fluoride were used, there would be no way to prove conclusively whether the alkyl fluoride participated directly in the reaction, or not. Reaction 2 is not reversible because the propane formed contains no tertiary hydrogen to undergo hydrogen exchange. Carbonium ions do not react with normal paraffins under the conditions of these experiments.¹

This conception of the mechanism leaves unexplained the relation between the amount of boron trifluoride charged and the total amount of reaction

obtained. It was primarily to investigate this aspect of the reaction that the present work was undertaken.

Experimental

Apparatus.—The apparatus used consisted of a gas handling system in calibrated sections of which the reagents and gaseous products were measured, a low-temperature reactor in which the reaction was conducted and a low-temperature fractionating column for separation of the gaseous products from the normally liquid products.

All of the reactions at low temperatures were performed in a glass reactor which consisted of a cylindrical vessel surrounded by a jacket in which liquid nitrogen was vaporized. By this means the temperature could be reduced well below -100° . This jacket in turn was completely surrounded by an evacuated jacket for heat insulation. The reactor was attached by means of a 45/50 standard taper joint to the top, through which a thermocouple well, a stirrer and a gas inlet tube entered the reactor. A vacuum-jacketed reflux condenser, cooled with solid carbon dioxide, was sealed to the vent from the reactor and was followed by a trap which could be cooled with solid carbon dioxide or liquid nitrogen and an absorption tube filled with sodium calcium hydrate.

The reactor was also used as the stillpot on the low-temperature distillation column in which the gaseous products were distilled from the liquid reaction products. For this purpose, hot air was passed through the jacket of the reactor to boil the charge.

Reagents.—The isobutane used was supplied by the Matheson Company and was C.P. grade, 99% pure or better. It was used without further purification. The boron trifluoride was also supplied by the Matheson Company and was claimed to be 97% pure or better. It was used as received.

The isopropyl fluoride was prepared by adding hydrogen fluoride to propylene according to the procedure described by Grosse and Linn.³ The product was distilled, discarding the first and last 10%. No propylene could be detected by infrared analysis in the fraction retained for use.

Technique.—The reactor was attached to the high-vacuum system and the isobutane and *i*-propyl fluoride were measured as gases in calibrated sections of the apparatus and were then condensed, in the reactor. The boron trifluoride was measured as a gas and was forced by mercury displacement into the liquid reaction mixture at -80° .

(1) A. Schneider and R. M. Kennedy, *THIS JOURNAL*, **73**, 5017 (1951).

(2) F. D. Bartlett, F. E. Coulton and A. Schneider, *ibid.*, **66**, 1531 (1944).

(3) A. V. Grosse and C. B. Linn, *J. Org. Chem.*, **3**, 26 (1939).

TABLE I
 SUMMARY OF ISOBUTANE SELF-ALKYLATION EXPERIMENTS AT -80°

Experiment No.	1	2	3	4	5	6	7	8
Reactants:								
Isobutane, mole	0.970	0.957	0.980	0.990	0.983	0.961	0.977	0.972
Isopropyl fluoride, mole	0.102	0.089	0.103	0.102	0.102	0.102	0.123	0.039
Boron trifluoride, mole	0.102	0.052	0.046	0.042	0.031	0.020	0.010	0.052
Total grams charged	69.5	64.5	66.4	66.6	65.4	63.4	64.9	62.3
Products:								
Gas, grams ^a	52.6	46.6	47.2	51.2	53.1	51.3	64.2	51.8
Liquid, grams ^b	9.5	12.0	10.9	11.0	8.5	0	3.0
Lower layer, grams ^c	7.1	1.0	2.1	3.1	1.4	1.6	1.9
Total grams recovered	69.2	59.6	59.2	65.5	61.4	66.2
Wt. % recovery	99.5	92.5	89.0	100	97.0	102
Composition of gas, mole %								
Propane	11.1	7.2	11.9	8.1	6.7	3.3	0	10.8
Isopropyl fluoride	0	0	0	0	0	0	10.1	0
Isobutane	88.9	92.8	88.1	91.9	93.3	96.7	89.9	89.2
Moles propane formed	0.103	0.059	0.099	0.074	0.061	0.029	0	0.034
Moles isobutane consumed	0.141	0.205	0.240	0.155	0.124	0.104	0	0.098
Isopropyl fluoride converted to propane, %	100	66	96	72	60	28	0	87
Isopropyl fluoride consumed, %	100	100	100	100	100	100	9.7	100

^a Consisted of propane, unreacted isopropyl fluoride, if any, and isobutane. ^b Consisted of normally liquid hydrocarbons boiling from 25° and up, chiefly 2,2,4-trimethylpentane. ^c Composed mainly of HF and BF_3 , with some hydrocarbon.

While the boron trifluoride was being admitted, a yellow viscous lower layer formed which settled rapidly when the stirrer was stopped. The reaction was complete as soon as all the boron trifluoride was added, but the reaction mixture was usually allowed to stir for about 15 minutes. During this time, the reflux condenser and the traps of the distillation column were charged with solid carbon dioxide. The stirrer was then stopped and the lower layer was separated and weighed. The reactor was cooled to about -100° and transferred rapidly to the distillation column. Ten ml. of *n*-pentane was pipetted into the column through the thermometer joint to act as a chaser and prevent the loss of isobutane as holdup in the column. The propane, isobutane and any unreacted isopropyl fluoride were distilled off, a single cut being taken to a vapor temperature of $+10^{\circ}$. The residue was cooled, weighed and charged to a concentric tube distillation column in which the alkylate was fractionated. In this column the distillation was continued till the vapor temperature reached 200° . Fractions of 0.5-ml. volume were collected which were analyzed for individual hydrocarbons by means of their infrared spectra. Details of the spectroscopic analyses have been previously described.¹

The condensed gases from the low-temperature distillation column were evaporated into the vacuum system and the number of moles of distillate was calculated from the volume and pressure. The gas was condensed again, into a copper bomb, and was analyzed for its individual components by means of its infrared spectrum.

Experimental Results

Eight successful runs were made at -80° using about 1.0 mole of isobutane. In seven of them, 0.10 ± 0.02 mole of isopropyl fluoride was used. In the eighth experiment, only 0.039 mole of fluoride was used. The amount of boron trifluoride varied from 0.01 to 0.10 mole, and is a very important variable. In two experiments, No. 1 and 8, the moles of boron trifluoride charged are substantially greater than one-half the moles of isopropyl fluoride charged. This is considered sufficient reason to set these experiments apart from the others in their interpretation. Experiment 2 has slightly more boron trifluoride than one-half the moles of isopropyl fluoride but is included with the other experiments.

Table I summarizes the experimental data showing the moles of each component charged and the products recovered, along with the composition of the recovered gases. Also tabulated are calculated quantities significant to the interpretations of the results "Moles Propane Formed," "Moles Isobutane Consumed," etc.

Discussion of Experimental Results

With a constant isopropyl fluoride concentration, the amount of isobutane consumed increases as the boron trifluoride concentration increases. This is shown graphically in Fig. 1. Within the experimental error of the analysis, the points fall on a straight line with a slope of four, *e.g.*, four moles of isobutane are consumed per mole of boron trifluoride charged.

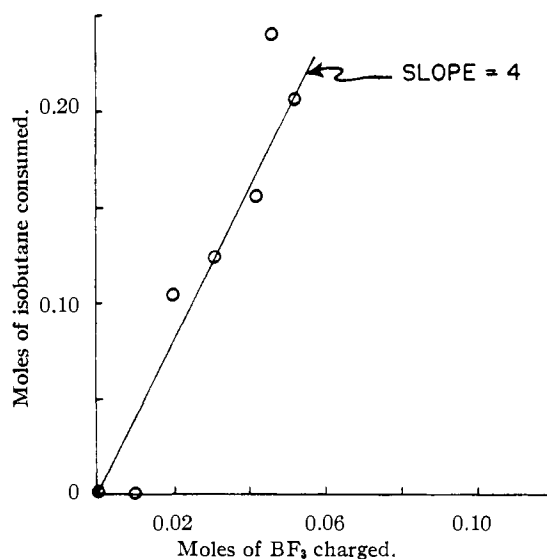


Fig. 1.—Moles of isobutane consumed per mole BF_3 .

The number of moles of propane formed per mole of boron trifluoride is shown graphically in Fig. 2. Except for Expt. 2, the points fall on a straight line with a slope of 2. Where excess boron trifluoride, *i.e.*, excess over an initial ratio of 2 moles of isopropyl fluoride to 1 of boron trifluoride is en-

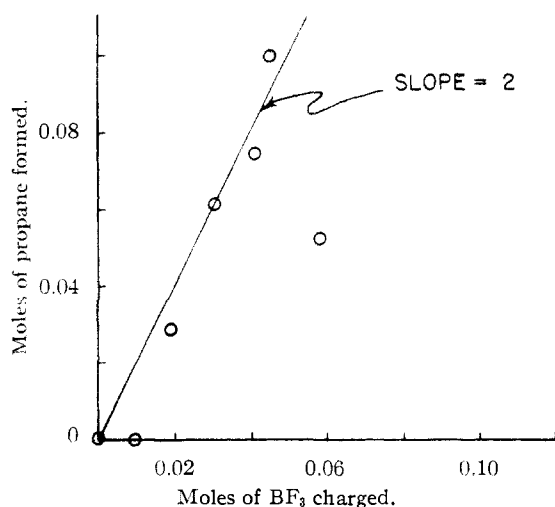
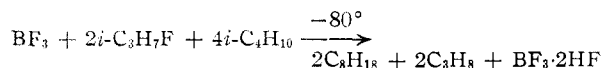


Fig. 2.—Moles of propane formed per mole of BF_3 .

ployed (Expts. 1 and 8) the points are far off the curve. It is concluded from this that 0.5 mole of boron trifluoride per mole isopropyl fluoride is sufficient to convert all the isopropyl fluoride to propane, and any boron trifluoride beyond this amount is unused in the reaction. As the moles of boron trifluoride charged approaches one-half of the initial isopropyl fluoride concentration, the percentage of isopropyl fluoride converted to propane approaches 100 on a straight line function. Once 100 per cent. has been reached, more boron trifluoride can have no effect, as shown by Expts. 1 and 8.

Unreacted isopropyl fluoride was never recovered in the reaction products even when less boron trifluoride than the amount required to consume all of the isopropyl fluoride was used. The unreacted fluoride is believed to be dissolved in the lower layer with which it is removed after the reaction is complete. This conclusion is supported by the stepwise manner in which the experiments were conducted. Boron trifluoride was added in increments of 0.01 mole and enough time was allowed between the additions for each stage of the reaction to subside. If the alkyl fluoride were consumed upon addition of the first increment of boron trifluoride there could be no further reaction as successive additions were made and the same amount of reaction would have been obtained regardless of the amount of boron trifluoride used. Consequently, the unreacted alkyl fluoride must be present as such during the intermediate stages of the reaction. Since it was never detected in the hydrocarbon products, it is concluded that it was removed with the lower layer.

From the ratios indicated by Figs. 1 and 2, it is to be expected that for every mole of propane formed, 2 moles of isobutane are consumed. This result was also predicted (1) from a consideration of the probable mechanism of the self-alkylation reaction and can therefore be considered as partial experimental confirmation of the proposed mechanism. The complete self-alkylation reaction can therefore be written as



It is a necessary conclusion from equations 1 to 5, assuming that one-half the *t*-butyl carbonium ions react *via* 3 and the other half react *via* 4, that two moles of isobutane are consumed per mole of propane formed. However, the observation that one mole of boron trifluoride converts exactly two moles of isopropyl fluoride to propane is an unexpected result. If the boron trifluoride were regenerated in a catalytically active form after reacting with each successive molecule of isopropyl fluoride, only catalytic quantities would be required to complete the reaction and the number of moles of isopropyl fluoride converted per mole of boron trifluoride charged would be very large. If it were not regenerated in a catalytically active form, the one to one ratio required by equations 1 to 5 would be expected. The existence of the two to one ratio indicates⁴ that a complex, $\text{BF}_3 \cdot 2\text{HF}$, catalytically inactive at -80° , is formed by the union of one mole of boron trifluoride with the hydrogen fluoride liberated from two moles of isopropyl fluoride. This complex has been reported by Hantzsch⁵ who prepared it by passing gaseous boron trifluoride into hydrogen fluoride in a reactor immersed in an ice-bath. The compound is an unstable solid which dissociates into its components and fumes in moist air. The solid melts at $56\text{--}58^\circ$. It is believed that at -80° this compound is insoluble in the reaction mixture. Since it can be formed only after two moles of isopropyl fluoride have liberated two moles of HF, the reaction proceeds to that point and then stops.

At higher temperatures the complex dissociates, and boron trifluoride is regenerated in a catalytically active form. At 0° , as much as 7.5 moles of isopropyl fluoride can be converted and 15 moles of isobutane consumed per mole of boron trifluoride charged.⁶

NORWOOD, PENNSYLVANIA

(4) Suggested by Prof. H. C. Brown, Dept. of Chemistry, Purdue University.

(5) A. Hantzsch, *Ber.*, **63B**, 1789 (1930).

(6) Unpublished data of this Laboratory.