SHORT COMMUNICATIONS

Complex of Boron Fluoride with Olefin on the Low-temperature

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In our recent paper[1] we showed by the measurements of isotopes effect that boron trifluoride can form the complexes with chloro- and chlorodifluoromethane only at the low-temperature. In the present work the possibility of the presence of complexes of boron trifluoride with olefins was examined by the same method and the relation of them with the mechanism of the boron trifluoride catalyzed polymerization reaction is discussed. Propylene was chosen as an olefin, being suitable for our purpose, because it was found against Booth's claim[2] that a well-purified boron trifluoride - propylene mixture is condensed together at −112°C (m. p. of carbon disulfide) without polymerization, but only the passage of moist air through its mixture can initiate polymerization.

We measured the equilibrium constants for isotopic exchange between boron trifluoride gas and boron trifluoride in propylene solution at −112°C and −96.5°C (m. p. of cumen) in a shaking type gas-liquid contactor, used in a previous work[1]. The two phases of boron trifluoride gas and propylene solution of boron trifluoride were kept in a glass flask, which was vigorously shaken in the low-temperature bath

TABLE I. EQUILIBRIUM CONSTANT FOR BORON ISOTOPE EXCHANGE BY BORON TRIFLUORIDE-PROPYLENE SYSTEM

Temp. °C	Mole ratio of propyrene to BF_3 in the liquid phase	Vapor press. mmHg	Equilibrium constant $\left[\frac{^{10}B}{^{11}B}\right]_{liq} \Big/ \left[\frac{^{10}B}{^{11}B}\right]_{gas}$
−112	0	300	1.011 ± 0.002
−112	0.05, 1, 3	—	—*
−112	4	95	1.021 ± 0.003
− 96.5	0	(1000)	(1.007)**
− 96.5	0.05, 1, 2.3	—	—*
− 96.5	3.4	400	1.016 ± 0.003
− 96.5	5.3	310	1.016 ± 0.003

* Solid
** Obtained by extrapolation from values at other temperatures

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[1] R. Nakane and O. Kurihara, *Sci. Papers Inst. Phys. Chem. Research* (*Tokyo*), **56**, 161 (1962).

[2] H. Booth and D. Martin, "Boron Trifluoride and its Derivatives", John Wiley & Sons, Inc., New York (1949), p 42.

for several hours. The equilibrium constant could be determined by measuring the $^{10}B/^{11}B$ ratio in the gas phase before and after equilibrations on a mass spectrometer, since a large excess of boron trifluoride was used in the liquid phase and hence the isotopic composition in the liquid phase remained practically unchanged throughout the experiments. On warming to room temperature after the experiments, the mixture, when evaporated, leaving only a trace amount of polymer on the vessel wall.

Results are shown in Table I. The equilibrium constant at −112°C on no propylene in the liquid phase was also secured. In this case, isotopic exchange occurs between gaseous boron trifluoride and liquid boron trifluoride as follows;

$$^{10}BF_3(gas) + {}^{11}BF_3(liq) \overset{K}{\rightleftharpoons} {}^{11}BF_3(gas) + {}^{10}BF_3(liq)$$

$$K=\frac{[^{10}BF_3(liq)]}{[^{11}BF_3(liq)]}\bigg/\frac{[^{10}BF_3(gas)]}{[^{11}BF_3(gas)]}=1.011\pm0.002\ (-112^\circ C)$$

Thus, this constant is identical with the vapor pressure ratio of isotopic molecules, $^{11}BF_3$ and $^{10}BF_3$.

We found that the values of the equilibrium constants were much larger when there was propylene in the liquid, than the value when there was no liquid propylene, as in the case of boron trifluoride-chloromethane and boron trifluoride-chlorodifluoromethane systems. These results show that isotopic exchange occurs between gaseous boron trifluoride and a new liquid compound, being quite different from liquid boron trifluoride, because the equilibrium constant for isotopic exchange is well correlated with the translational, rotational and vibrational energy states of molecules. Boron trifluoride is known to coordinate with many compounds and the equilibrium constants for isotopic exchange between these liquid complexes and gaseous boron trifluoride are always larger than the vapor pressure ratio of isotopic molecules. Therefore, we consider that its new liquid compound is the complex of boron trifluoride with propylene, and isotopic exchange is shown by following equation;

$$^{10}BF_3(gas) + {}^{11}BF_3\cdot CH_2CHCH_3(liq) \overset{K}{\rightleftharpoons} {}^{11}BF_3(gas) + {}^{10}BF_3\cdot CH_2CHCH_3(liq)$$

$$K=\frac{[^{10}BF_3\cdot CH_2CHCH_3(liq)]}{[^{11}BF_3\cdot CH_2CHCH_3(liq)]}\bigg/\frac{[^{10}BF_3(gas)]}{[^{11}BF_3(gas)]}=1.021\pm0.003\ (-112^\circ C)$$

Although Evans et al.[3] claimed in their investigation on the mechanism of the polymerization that boron trifluoride did not form a stable complex with isobutylene, our result suggests that Evans' conclusion is wrong and the complex, $BF_3\cdot CH_2C(CH_3)_2$, can also exist at low-temperature.

However, these liquid complexes are stable only at low-temperature, because it was found that the solubility of boron trifluoride in propylene solution decreased markedly with the increase in temperature and, for example, boron trifluoride could scarcely be dissolved into liquid propylene even at −78°C.

For comparison, the system of boron trifluoride and paraffin such as propane was also investigated and it was found that the two liquids are practically immiscible at −96.5°C or −112°C. Therefore the formation of any complex can not be considered.

Thus, we could detect the formation of the stable liquid complexes of boron trifluoride with an unsaturated hydrocarbon such as propylene at the low-temperature, and would like to conclude that these stable complexes have no concern with the mechanism of the polymerization and are not the intermediate products for polymerization, because the polymerization of both propylene and isobutylene can not proceed as long as there is no co-catalyst such as water, albeit the complexes can exist always at the low-temperature.

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[3] A. Evans and M. Polanyi, *J. Chem. Soc.*, **1947**, 253.