fairly constant radiation baseline. The samples were mulled to a paste with nujol mineral oil which was spread in a thin film between two rock salt plates

Certain corrections were made in the curves to give them a more polished appearance. Minor bands due to atmospheric carbon dioxide and water have been eliminated. The bands marked with asterisks are made up in good part of nujol absorption.

LAWRENCE, KANSAS RECEIVED JUNE 26, 1951

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF WAYNE UNIVERSITY AND THE DEPARTMENT OF CHEMISTRY OF PURDUE UNIVERSITY]

The Action of the Catalyst Couple Aluminum Chloride–Hydrogen Chloride on Toluene at Low Temperatures; the Nature of Friedel–Crafts Complexes[1,2]

BY HERBERT C. BROWN[3] AND HOWARD W. PEARSALL[4]

In the absence of hydrogen chloride and at low temperatures (−80°), purified aluminum chloride neither interacts with nor dissolves appreciably in toluene. In the presence of excess hydrogen chloride, the aluminum chloride dissolves in the toluene to give a clear solution, a brilliant green in color. From the decrease in pressure of the hydrogen chloride, it appears that one mole of the gas is taken up per mole of $AlCl_3$ which goes into solution. The reaction is reversible; that is, removal of the hydrogen chloride precipitates the aluminum chloride and the toluene is recovered unchanged. The reaction is believed to involve the formation of a carbonium ion salt of the hypothetical acid, $HAlCl_4$: $CH_3C_6H_5 + HCl + {}^1/_2Al_2Cl_6 = [CH_3C_6H_6]^+[AlCl_4]^-$. At −45.4° one mole of hydrogen chloride is taken up for each two moles of $AlCl_3$: $CH_3C_6H_5 + HCl + Al_2Cl_6 = [CH_3C_6H_6]^+[Al_2Cl_7]^-$. The complexes which form in the course of Friedel–Crafts reactions are believed to be carbonium ion salts of this kind. It is proposed that the high solubility of aluminum halides in these Friedel–Crafts complexes is due to the formation of a series of higher complexes of this kind, with the general formula $R^+[AlX_4 \cdot nAlX_3]^-$. It is further proposed that these complexes play an important role in most Friedel–Crafts reactions by furnishing a highly polar medium in which the ionic intermediates may form and react.

Introduction

The alkylation of aromatic hydrocarbons, catalyzed by aluminum chloride and similar Friedel–Crafts catalysts, is ordinarily accompanied by the formation of deeply colored oily liquids of high density. In spite of considerable study, the precise nature and function of these "Friedel–Crafts complexes" are not well understood.[5] In the hope of throwing some light on the composition of these materials, a study was undertaken of the interaction of toluene, aluminum chloride, and hydrogen chloride at low temperatures, utilizing techniques which permitted following the pressure of hydrogen chloride as a function of composition.

Results

In the absence of hydrogen chloride, no reaction was observed between purified aluminum chloride and toluene. Five ml. of toluene was placed over 0.35 g. of aluminum chloride. In 22 hours at −80°, no change was observed. At −45° no color was noticed in 1 hour, and only a slight yellow coloration appeared after several additional hours. Finally, the sample was maintained at 0° for 20 hours. Again only a faint yellow color was observed. The toluene, removed from the sample, gave values for the vapor pressure (6.8 mm. at 0°) and refractive index ($n^{25}D$ 1.4938) identical with the original sample of toluene.

Traces of water markedly altered the results. Thus, repetition of the experiment utilizing 0.35 g. of aluminum chloride to which had been added 6.6 mg. of water led to the development of marked colors. In 1 hour at −45° the aluminum chloride, pure white at the start, had become definitely colored, varying in spots from a light yellow to an intense canary yellow.

The action of hydrogen chloride was particularly interesting. At −80° aluminum chloride is not noticeably soluble in toluene, but subsequent addition of hydrogen chloride causes the aluminum chloride to dissolve. At the same time the toluene solution becomes a brilliant green in color. The reaction is reversible. Removal of the hydrogen chloride by distillation precipitates solid aluminum chloride. Re-addition of hydrogen chloride causes the aluminum chloride to redissolve, again giving the green solution. The cycle has been repeated as many as four times without evidence of irreversible changes. All of the components can be recovered quantitatively by distillation of the hydrogen chloride and toluene from the less volatile aluminum chloride.

The solution of the aluminum chloride was accompanied by a decrease in the hydrogen chloride pressure, and it was of interest to establish a quantitative relationship here. Unfortunately we encountered experimental difficulties which greatly affected the precision of the results. In addition to the usual difficulties involved in introducing small accurately weighed samples of anhydrous aluminum chloride into the vacuum apparatus, we discovered that equilibrium in these reactions is attained very slowly, frequently requiring days or even weeks. The devices we adopted for maintaining a constant temperature at −80° for extended periods of time did not prove very satisfactory. As a result, the precision we attained leaves much to be desired. However, the data do indicate, albeit only roughly, the ratio of aluminum chloride to hydrogen chloride in the green solution.

In a typical experiment 0.36 mmole of aluminum

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(1) The Catalytic Halides. II.

(2) Presented before the Division of Physical and Inorganic Chemistry at the New York Meeting of the American Chemical Society, September, 1947.

(3) Department of Chemistry, Purdue University.

(4) Standard Oil Company (Indiana) Fellow at Wayne University, 1945–1947.

(5) A summary of earlier work is contained in C. A. Thomas, "Anhydrous Aluminum Chloride in Organic Chemistry," A. C. S. Monograph No. 87, Reinhold Publishing Corp., New York, N. Y., 1941, pp. 48–54.

chloride (as $AlCl_3$) was caused to dissolve in 18.6 mmoles of toluene by 6.60 mmoles of hydrogen chloride. The reaction was slow; some six days were required for complete solution. The solution was a clear green. The original pressure of the hydrogen chloride above the toluene, 76.6 mm. at −84.1°, decreased over several days to observed limiting values of 71.4–71.8 mm. If the solubility of hydrogen chloride in the dilute solution of the complex in toluene may be considered to be the same as the solubility of hydrogen chloride in the pure solvent, then a total of 0.38–0.42 mmole of hydrogen chloride was absorbed to form the complex (Fig. 1). Within the admittedly poor precision of these experiments, it follows that one mole of hydrogen chloride reacted per mole of monomeric aluminum chloride in solution.

At lower pressures of hydrogen chloride the color changes to yellow. On standing, white crystals, presumably aluminum chloride, separate from the solution. The decrease in pressure of hydrogen chloride observed in this range corresponds to higher ratios of $AlCl_3$:HCl. These ratios vary, and appear to be a function of the concentration of hydrogen chloride (Fig. 1). Thus the 1:1 ratio apparently represents a limiting value attained only at relatively high concentrations of hydrogen chloride.

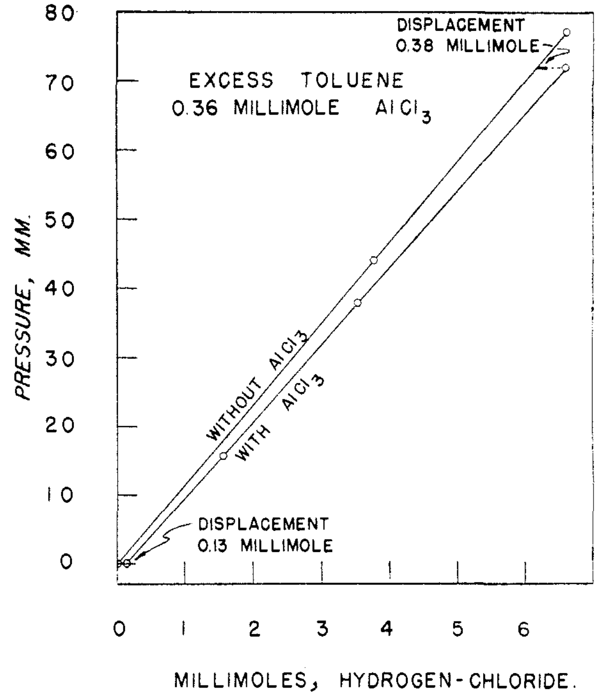


Fig. 1.—Pressure of hydrogen chloride at −84.1° in presence and absence of aluminum chloride.

If the green solution at −84.1° is permitted to warm up to −45.4°, the solution becomes yellow in color. Removal of the hydrogen chloride by distillation precipitates aluminum chloride as before, and the toluene is not noticeably altered. The components can be quantitatively recovered (within 0.2%). Therefore, whatever is at the basis of the changes in color, permanent chemical changes in the individual components are not involved. At this temperature the decrease in pressure of hydrogen chloride corresponds quite closely to the existence of a complex containing aluminum chloride and hydrogen chloride in the ratio $2AlCl_3$:1HCl. This ratio, moreover, appears to be relatively insensible to changes in hydrogen chloride pressure (Fig. 2).

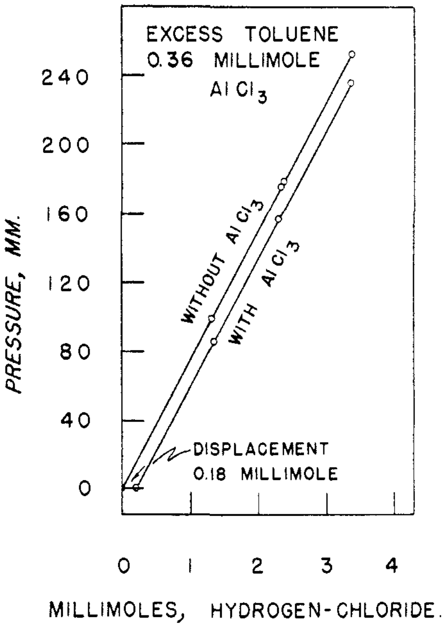
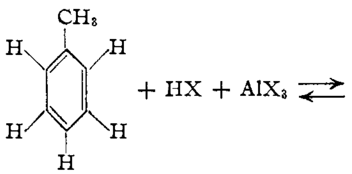


Fig. 2.—Pressures of hydrogen chloride at −45.4° in presence and absence of aluminum chloride.

Discussion

Friedel–Crafts complexes[5] appear to involve an aromatic hydrocarbon (or certain unsaturated hydrocarbons not considered in this study), aluminum halide and hydrogen halide. They are characterized by intense colors, high conductivity, and excellent solvent properties for aluminum halides and polar substances.[6] In those instances where definite products have been characterized, the ratios of aluminum halide (AlX_3) to hydrogen halide are apparently 1:1 and 2:1.

It is proposed that these Friedel–Crafts complexes are organic salts of the hypothetical acids,[7] $HAlX_4$ and HAl_2X_7, in which the aromatic hydrocarbon functions as a base



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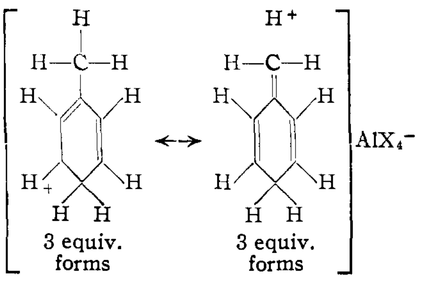
(6) Recently several authors [V. A. Plotnikov and N. N. Gratsianskii, *Bull. acad. sci., U. S. S. R., Classe sci. chim.*, 101 (1947); *C. A.*, **42**, 4480 (1948), and R. E. Van Dyke, THIS JOURNAL, **72**, 3619 (1950)] have reported evidence that aluminum bromide forms complexes with simple benzenoid hydrocarbons. These complexes are relatively unstable and do not conduct electricity. They are probably quite different from the Friedel–Crafts complexes under discussion here, and may be only crystal lattice compounds without independent existence in solution.

(7) H. C. Brown and H. W. Pearsall, *ibid.*, **73**, 4681 (1951).



The concept that aromatic hydrocarbons possess basic properties sufficiently strong to form salts with hydrogen halide–aluminum halide and similar reagents suggests that such reagents could be utilized to extract, preferentially, more strongly basic aromatic hydrocarbons from those less basic. McCaulay, Shoemaker and Lien[8] have recently demonstrated that hydrogen fluoride–boron trifluoride can be readily utilized to extract the more basic *m*-xylene from its mixture with the less basic *o*- and *p*-xylene isomers.

These authors establish the ratio $Ar:BF_3 = 1:1$ in the complexes formed from aromatic hydrocarbons, boron trifluoride and hydrogen fluoride, the latter being present in excess as the solvent. Our own work establishes the limiting ratio $AlCl_3:HCl = 1:1$, the aromatic hydrocarbon being present in excess as the solvent. Consideration of both studies, then, leads to the composition $1Ar:1MX_3:1HX$ for the limiting ratio of the three components in the Friedel–Crafts complexes.

It is well known that aluminum chloride is readily soluble in these Friedel–Crafts complexes and that such concentrated solutions are frequently used commercially to catalyze Friedel–Crafts reactions. The high solubility of aluminum chloride probably involves the formation of complexes of higher order than the simple 1:1 union. In other words, it is proposed that a series of complexes exists, corresponding to the compositions

$$ArH^+\,AlX_4^-,\ ArH^+\,Al_2X_7^-,\ ArH^+\,Al_3X_{10}^-,\ ArH^+,\ Al_4X_{13}^-,\ \text{etc.}$$

The relationship is probably similar to that which obtains when sulfur trioxide is added to water. The parent acid may be represented as $H_2O{\cdot}SO_3$; further addition of sulfur trioxide results in a series of higher acids, a number of which have been identified[9]

$$H_2SO_4,\ H_2S_2O_7,\ H_2S_3O_{10},\ H_2S_4O_{13},\ \text{etc.}$$

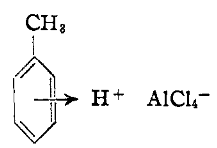
Moreover, just as the addition of sulfur trioxide to sulfuric acid increases the acidity of the solution,[10] it is probable that a Friedel–Crafts complex containing dissolved aluminum halide exhibits increased acidity.

This interpretation permits a simple explanation for the observation that at low temperatures (−80°) and relatively high hydrogen chloride concentrations the $AlCl_3:HCl$ ratio was essentially 1:1, but became 2:1 at higher temperatures and somewhat lower concentrations of hydrogen chloride.

The interpretation also permits a reasonable explanation of the numerous reports[5,11] that aluminum halides and aromatic hydrocarbons do not react to form complexes in the absence of hydrogen halide, yet after complexes are precipitated with the aid of halogen acids, examination of the products frequently reveals the absence of the acid. It is probable that halogen acids are present, but in relatively minor amounts and thus escape identification in the analysis of the relatively crude products. Only a small quantity of hydrogen halide would be required to maintain a large quantity of aluminum halide in solution in the form $ArH^+Al_nX_{3n+1}^-$, if n is relatively large. It is significant that in the present investigation, where the technique permitted quantitative recovery of the hydrogen chloride, its quantitative removal led to complete destruction of the complex and to the formation of analytically pure toluene and aluminum chloride.

Finally, we wish to suggest that such complexes play an important part in Friedel–Crafts reactions.[12] The generally accepted mechanism of the Friedel–Crafts reaction involves the slow formation of carbonium ions, followed by a rapid attack of the ions on the aromatic nucleus. However, all discussions of the Friedel–Crafts reaction ignore the difficulty of forming these ionic intermediates in the non-polar media (carbon bisulfide, excess hydrocarbon, etc.) in which the reactions are commonly carried out. This lack of a polar medium must be largely responsible for the induction period which is frequently noted,[13] for as soon as the complex phase appears, the reaction proceeds with great rapidity. Since the complex phase is a highly polar medium capable of dissolving excess aluminum halide, alkyl halide and aromatic hydrocarbon, the formation of the ionic intermediates and their further reaction are both facilitated. Therefore, these complexes should not be considered in the nature of unimportant by-products of the Friedel–Crafts reaction, but as important constituents of the reaction as it is ordinarily carried out.

In this paper the conjugate acids of the aromatic hydrocarbons have been represented as carbonium ions. Dewar has proposed that such products should be represented as π-complexes[14]



However, there is now available considerable evidence which renders the π-complex representation less preferable than that proposed in the present paper—a structure in which the proton is definitely united to one of the ring atoms, predominantly in positions ortho and para to the

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[8] D. A. McCaulay, B. H. Shoemaker and A. P. Lien, *Ind. Eng. Chem.*, **42**, 2103 (1950). See also D. A. McCaulay and A. P. Lien, THIS JOURNAL, **73**, 2013 (1951).

[9] D. J. Miller, *J. Chem. Soc.*, 2589 (1950).

[10] L. P. Hammett and A. J. Deyrup, THIS JOURNAL, **54**, 2721 (1932).

[11] J. F. Norris and D. Rubinstein, *ibid.*, **61**, 1163 (1939); J. F. Norris and J. N. Ingraham, *ibid.*, **62**, 1298 (1940); J. F. Norris and J. E. Wood, *ibid.*, **62**, 1428 (1940).

[12] H. C. Brown, H. Pearsall and L. P. Eddy, *ibid.*, **72**, 5347 (1950).

[13] G. Gustavson, *J. prakt. Chem.*, [2] **68**, 209 (1903).

[14] M. J. S. Dewar, *J. Chem. Soc.*, 406 (1946), and private communication.

methyl group. This question will be treated in a subsequent paper.

Experimental Part

Apparatus and Materials.—All experiments were carried out in an all-glass high vacuum apparatus in which the reactants came in contact only with glass and mercury.

Sulfur-free reagent-grade toluene (Eastman Kodak Company) was purified by codistillation with 10% by volume of methyl ethyl ketone[15] in a column rated at 50 theoretical plates. The product from this treatment was again fractionated with the column and a number of constant boiling fractions were collected. Cooling curves were run on these fractions. All showed long, flat plateaus at −94.8° with sharp breaks at the ends, as compared with the literature value[16] of −95.032°. The refractive index was $n^{25}\mathrm{D}$ 1.4938, as compared to the literature value,[16] $n^{25}\mathrm{D}$ 1.49405. The best samples were dried with Drierite and introduced into the vacuum apparatus where they were stored in a tube containing a sodium mirror on the walls. The vapor pressure exhibited by the toluene at 0° remained unchanged at 6.8 mm. as portions of the material were distilled away. In contrast, a sample of toluene to which 2.5% of benzene and *m*-xylene were added, showed marked changes in vapor pressure under this treatment. Study of the homogeneity of the vapor pressures of recovered toluene was adopted as a convenient means of testing for changes in the toluene occurring in the course of the experiments. Samples of toluene were measured as liquid in a tube of calibrated volume.

Reagent-grade powdered aluminum chloride (J. T. Baker and Company) was placed in one end of a long 25-mm. Pyrex tube in an atmosphere of prepurified nitrogen. The tube was maintained in a tube furnace for a period of three days at a temperature of 125°. A mass of large, white crystals formed on the cool portion of the tube projecting out of the furnace, while a considerable volume of gray powder remained behind. The tube was cooled, opened, and the crystalline sublimate quickly transferred with a porcelain spatula into weighing bottles. These were stored in a desiccator.

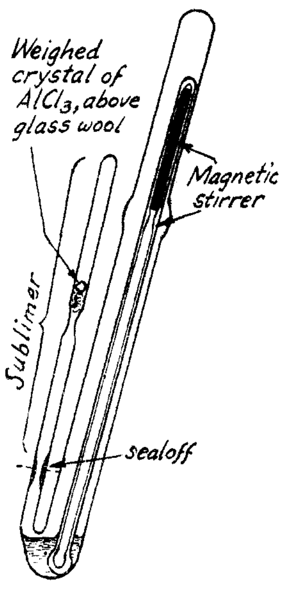

Fig. 3.—Side view of reaction vessel used for study of toluene–hydrogen chloride–aluminum chloride system at low temperatures.

After many trials the following procedure[17] was found most satisfactory for introducing the aluminum chloride into the sample tube (Fig. 3). (The sample tube was inclined as shown to improve agitation and to minimize the danger that the magnetically operated rod would break through the bottom of the tube.) A piece of the sublimed aluminum chloride, weighing approximately 0.5 g., was transferred with glass tongs from a tared weighing bottle to the open-side arm. The tube was then sealed by heating at a point considerably below the open end to avoid introduction of water from the flame. The system was thoroughly evacuated. Crude funnels of asbestos paper were temporarily wired around the base of the U-shaped tubes which flank the sample tube on both sides, and in the funnels was placed a small quantity of Dry Ice. This prevented mercury vapor from condensing in the sample tube during the subsequent step.

A beaker containing small pieces of Dry Ice was raised around the bulb of the reaction tube. A tubular electric heater was slipped down over the side tube containing the aluminum chloride and gentle heat applied—so that, in the course of an hour, one-third to one-half of the aluminum chloride in the sublimer appeared in the cooled bulb of the reaction tube.[18]

The side tube was sealed at the constriction, pulled away, cooled and carefully opened by a technique which allowed dry air to enter slowly. The aluminum chloride was then shaken out into a tared vessel and weighed. The difference between the initial and final weights equaled the weight of material entering the reaction tube; 96% of this weight was assumed to represent sublimed aluminum chloride actually in the reaction vessel, since several test experiments showed a loss of 2–6%. (This loss is presumably due to traces of water, hydrogen chloride, and mechanical entrainment of small amounts of unsublimed material in the small plug of glass wool.)

Hydrogen chloride, generated from C.P. hydrochloric acid and concentrated sulfuric acid was fractionated in the vacuum apparatus by alternately pumping at −196° and vaporizing through a trap at −112°. The center-cut sample, tensiometrically homogeneous at −112°, was stored in a large bulb. It was measured as a gas in a calibrated bulb and transferred to a bulb in the "stopcock system." Hydrogen chloride was transferred to and from the sample tube through a stopcock and the quantity present in the sample tube was determined from the decrease in pressure of the gas remaining in the stopcock system.

TABLE I

EQUILIBRIUM PRESSURES OF HYDROGEN CHLORIDE IN PRESENCE OF EXCESS TOLUENE AT 84.1° WITH AND WITHOUT ALUMINUM CHLORIDE

Hydrogen chloride, mmole	Press., mm.	Temp., °C.	Press., mm. (cor. to −84.1°)	Remarks
Without aluminum chloride				
0.00	0.0	−84.1	0.0	18.6 mmoles toluene
3.89	42.8	−84.1	42.8	
6.60	77.6	−84.1	76.1	Solution colorless
With aluminum chloride (0.36 mmole $AlCl_3$)				
6.60	74.44	−83.8	73.9	After 132 hr. at −80°. Clear green solution
1.62	15.73	−83.3	15.3	Clear green solution
0.11	0.05	−83.5	0.1	After 0.6 hr., solution clear yellow
0.11	0.44	−83.5	0.4	After 4 hr., white solid ($AlCl_3$) formed
6.62	73.13	−83.5	71.8	Hydrogen chloride returned. Green solution with slight suspension of $AlCl_3$ after 30 min.
6.62	71.39	−84.1	71.4	After 13 hr., solid dissolves; clear green solution
6.62	71.15	−84.4	71.8	Hydrogen chloride removed, then returned
3.62	36.59	−84.1	36.6	
0.18	0.66	−78		After 10 min., clear yellow solution After 1 hr., white ppt. formed
.16	.26	−84.1	0.3	After standing 14 hr.
.13	.00	−84.1	0.0	Solution yellow with white ppt.

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(15) R. Ewell, J. Harrison and L. Berg, *Ind. Eng. Chem.*, **36**, 874 (1944).

(16) A. F. Forziati, A. R. Glasgow, Jr., C. B. Willingham and F. D. Rossini, *J. Research Natl. Bur. Standards*, **36**, 129 (1946).

(17) The procedure is adapted from that described by H. Pines and R. Wackher, THIS JOURNAL, **68**, 596 (1946).

(18) These precautions were adopted to avoid the reaction of aluminum chloride with hot glass. Such reaction was observed during attempts to transfer the aluminum chloride by heating with a flame.

Reaction of Hydrogen Chloride–Aluminum Chloride with Toluene.—Excess toluene, 18.6 ± 0.1 mmoles, was placed in the sample tube and cooled to $-84.1°$ (a solid-liquid slush of ethyl acetate was used). Measured amounts of hydrogen chloride were then introduced. After each addition, the equilibrium pressure in the system was noted. The data are given in Table I and define the line "without $AlCl_3$ at $-84.1°$" in Fig. 1. The contents of the tube were removed to storage and a small quantity of aluminum chloride, 0.36 ± 0.02 mmole as $AlCl_3$, was introduced into the reaction tube as described previously. The hydrogen chloride–toluene mixture was returned to the tube and the mixture maintained at $-80°$ with intermittent stirring for 6 days. By this time practically all of the aluminum chloride had dissolved. (A few minute crystals adhered to the glass walls above the surface of the solvent; however, by visual observation this represented a negligible fraction of the aluminum chloride introduced.) The $-84°$ bath was then raised and pressure readings taken until no change was observed. The equilibrium pressure in the presence of 6.62 mmoles of hydrogen chloride was 71.4–71.8 mm., considerably below the 76.6 mm. value obtained in the absence of aluminum chloride (Table I).

From the graphical representation of the data (Fig. 1), the decrease in pressure corresponds to a loss of hydrogen chloride of 0.38 mmole as compared to the 0.36 mmole of aluminum chloride introduced.

As indicated in Table I, the solution was a clear green in color. Removal of part of the hydrogen chloride caused a white solid (presumably aluminum chloride) to precipitate. Return of hydrogen chloride caused the aluminum chloride to dissolve, regenerating the green solution. Under these conditions decomposition of the complex is a relatively slow process. Thus removal of a large portion of the hydrogen chloride gave after 0.6 hour a clear yellow solution. After four hours, an increase in pressure had occurred and the solution had become cloudy with precipitated aluminum chloride (Table I).

The reactants were returned to the reaction tube and the temperature raised to $-45°$. Immediately a brown lower layer formed. Soon thereafter all the white solid had dissolved and the upper layer was bright yellow in color. The lower layer was very small. The equilibrium pressures were then determined in the usual manner as the amount of hydrogen chloride was varied. Results are summarized in Table II.

TABLE II

EQUILIBRIUM PRESSURES OF HYDROGEN CHLORIDE IN PRESENCE OF EXCESS TOLUENE AT $-45.4°$ WITH AND WITHOUT ALUMINUM CHLORIDE

Hydrogen chloride, mmoles	Press., mm.	Temp., °C.	Press., mm. (cor. to $-45.4°$)
Without aluminum chloride			
1.177	12.9	−45.9	13.2
1.331	97.7	−45.9	94.5
2.368	174.6	−45.9	176
3.385	253.5	−45.4	253.5
2.335	173.6	−45.4	173.6
With aluminum chloride (0.36 mmole $AlCl_3$)			
1.395	87	−45.4	87
2.339	159	−45.4	159
3.296	232	−45.4	232
0.177	0.0	−45.4	0.0

The decrease in pressure of hydrogen chloride (Fig. 2) corresponds to a ratio of $AlCl_3$ to HCl in the complex of 1.8:1. In a check experiment a ratio of 2.1:1 was obtained. Rapid removal of the hydrogen chloride at $-45°$ left 0.177 mmole of hydrogen chloride united with the 0.36 mmole of aluminum chloride, a ratio of 2.0:1 (Table II). Additional hydrogen chloride is given off only very slowly at this temperature, more rapidly at higher temperatures.

A total of 8.176 mmoles of hydrogen chloride was recovered; 8.156 mmoles had been used, so the recovery was 100.2%. The toluene recovered was tensiometrically homogeneous and exhibited a vapor pressure of 6.8 mm. at 0°, identical with that of the original sample. The recovery was 99.8%. The aluminum chloride remaining in the tube had a slight yellow tinge; analysis by the method of Snyder[19] gave 0.365 mmole of aluminum.

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[19] L. J. Snyder, *Ind. Eng. Chem., Anal. Ed.*, **17**, 37 (1945).

LAFAYETTE, INDIANA RECEIVED JANUARY 10, 1951

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY]

Molecular Dimensions of Natural Rubber and Gutta Percha[1]

BY H. L. WAGNER AND P. J. FLORY

The unperturbed end-to-end dimensions $(\overline{r_0^2})^{1/2}$ of *cis*-polyisoprene (natural rubber) and *trans*-polyisoprene (gutta percha) have been determined from intrinsic viscosities measured at the limiting critical miscibility temperature (Θ) for $M = \infty$ in methyl *n*-propyl ketone and in *n*-propyl acetate, respectively. Several fractions of each polymer were used; molecular weights were determined osmotically. $K = [\eta]_\Theta/M^{1/2}$ is independent of M, in accordance with previous observations on a number of other polymer systems. The value of $(\overline{r_0^2}/M)^{1/2}$ calculated from K for gutta percha is about 25% greater than that for rubber. This is in approximate agreement with calculations based on the chain structure assuming free rotation. However, both polymers are appreciably more extended than would be predicted for free rotation, even in the absence of perturbations arising from polymer–solvent interaction.

Introduction

A method for the determination of characteristic dimensions of polymer molecules from appropriate viscosity measurements has been established in previous papers.[2-5] The following relationships are employed

$$[\eta] = KM^{1/2}\alpha^3 \qquad (1)$$

$$\alpha^5 - \alpha^3 = 2\psi_1 C_M (1 - \Theta/T)M^{1/2} \qquad (2)$$

$$K = \Phi(\overline{r_0^2}/M)^{3/2}$$

where $(\overline{r_0^2})^{1/2}$ is the root-mean-square distance from beginning to end of the chain *in the absence of perturbations due to interactions between remotely connected segments*, and α is the factor by which the actual root-mean-square distance $(\overline{r^2})^{1/2}$ exceeds this unperturbed distance in a particular solvent at a given temperature; K is a parameter which is characteristic of the polymer but independent of the solvent; and Φ is a hydrodynamic constant which

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[1] This investigation was carried out at Cornell University in connection with the Government Research Program on Synthetic Rubber under contract with the Office of Rubber Reserve, Reconstruction Finance Corporation.

[2] P. J. Flory, *J. Chem. Phys.*, **17**, 303 (1949).

[3] P. J. Flory and T. G. Fox, Jr., THIS JOURNAL, **73**, 1904 (1951).

[4] T. G. Fox, Jr., and P. J. Flory, *ibid.*, **73**, 1909 (1951).

[5] T. G. Fox, Jr., and P. J. Flory, *ibid.*, **73**, 1915 (1951).