[Contribution from the Chemical Laboratory of McGill University]

MOLECULAR ATTRACTION AND VELOCITY OF REACTIONS

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Received July 27, 1925 Published December 12, 1925

Introduction

In a previous paper[1] the reaction between liquid hydrogen bromide and liquid propylene was described. This investigation has been extended to include the system, hydrogen chloride-propylene, and it is the object of the present paper to discuss this reaction in relation to that involving hydrogen bromide. Particular attention is paid to the influence of the concentration of halogen hydride on the velocity of the reaction. An examination of the reaction in the gaseous state is also described. In conclusion, some ways in which temperature and pressure may affect the velocity of a chemical reaction are indicated.

Preparation of Reactants.—The propylene was prepared and purified by the method described in a previous paper.[2] The hydrogen chloride was generated by the action of sulfuric acid on sodium chloride. It was purified by leading it through sulfuric acid and phosphorus pentoxide tubes. It was condensed and distilled into the mixing apparatus as required.

Method of Mixing.—The method for obtaining a reaction mixture has been described in a previous paper[3] already referred to. It is worth emphasizing that the reactants are brought together in known quantities at the temperature of liquid air and sealed off in small glass bulbs. At no stage are the gases contaminated by air or moisture. Care was taken to choose bulbs of such a volume that they were almost completely filled with the liquid at the temperature of the reaction. The reaction time was taken from the moment the bulb was removed from the liquid air and placed in the thermostat (at 0° or 20°), to the moment when it was plunged back into the liquid air.

Analysis.—The method of analysis employed for hydrogen bromide and propylene could not be used for this reaction because of the relation of the solubility products of silver thiocyanate and silver chloride. A test experiment showed that the alkyl chlorides formed in the reaction (unlike the alkyl bromides) were not affected by a 0.1 *N* sodium hydroxide solution under the conditions of analyzing for unreacted hydrogen chloride. Sodium hydroxide with phenolphthalein as indicator was used in the titration; otherwise the procedure was the same as that previously described.[4]

In certain experiments involving a three-component mixture of hy-

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[1] Maass and Wright, This Journal, **46**, 2664 (1924).

[2] Maass and Wright, *ibid.*, **43**, 1098 (1921).

[3] Ref. 1, p. 2666.

[4] Ref. 1, p. 2667.

drogen chloride, hydrogen bromide and propylene, it was considered advisable to employ a method of analysis independent of sodium hydroxide or silver nitrate, both of which slowly attack the alkyl bromide, and so a method of analysis was devised depending on conductivity measurements. The contents of a bulb were dissolved in a definite volume of distilled water in amount such that, even if no reaction had taken place, the normality would not exceed 0.01 *N*. Since the equivalent conductivities of hydrobromic acid and hydrochloric acid are nearly the same and vary in a linear way at low concentrations, it was an easy matter to determine the amount of acid by means of a dip electrode which had been calibrated with acid solutions of known normality. This method does not distinguish between the two acids but gives within 1% the total amount of uncombined acid.

Products of the Hydrogen Chloride Reaction

The difficulty in making up large quantities of reaction mixture lies in the high vapor pressure of the liquid mixture which limits the size of the glass tube which can be used. About 30 cc. of the reaction mixture containing an excess of hydrogen chloride was allowed to react at room temperature for one month. This mixture was fractionated as previously described,[5] with this innovation, that the vapor pressures of the pure fraction, which was obtained in minute quantity, were measured by a method somewhat similar to that devised by Dennis, Corey and Moore.[6]

When the excess of hydrogen chloride had been driven off, the greater portion left distilled between 21 and 17 cm. pressure at 0°. This portion was redistilled and proved to be *iso*propyl chloride, as the following measurements show. At 0°, 10° and 20° the observed vapor pressures were 19.3, 29.7 and 43.3 cm., respectively, in agreement with the values given in the literature. For instance, at 20° the vapor pressure of *iso*propyl chloride is given as 43.55 cm., whereas that of the normal chloride is given as 28 cm. Furthermore, analysis of the compound gave 45.7% of chlorine which is within 0.5% of the calculated chlorine content.

The residue after the pressure had fallen to 17 cm., consisted of about 5 cc., a large portion of which was still *iso*propyl chloride. By a large number of fractionations the fractions of lowest vapor pressure (between 1 and 2 cm. at 0°) were obtained. These were found to have boiling points between 114° and 120°, the variation probably depending upon the presence of various small amounts of *iso*propyl chloride. Only a small quantity was available for analysis and the chlorine content of various samples was found to be 28, 22.5, 27 and 32.3%. The compound 2-methyl-4-chloropentane contains 29.5% of chlorine and has

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[5] Ref. 1, p. 2671.

[6] Dennis, Corey and Moore, This Journal, **46**, 667 (1924).

a boiling point in the neighborhood of 115°. Hence, as far as the authors can judge, the residue consisted of this compound. The products of the reaction, therefore, are similar to those obtained in the hydrogen bromide-propylene reaction, namely, *iso*propyl chloride and a chlorohexane.

The formation of the halogen hexane was unexpected, as pointed out in a previous paper.[7] In this connection it may be noted that a complex alkyl halide may be formed by the combination of several molecules of amylene and one molecule of hydrogen chloride.

Velocity of Reaction

No measurable reaction was found to take place in an equimolecular mixture of halogen chloride and propylene at —78.5°. The curves, Fig. 1, show the percentage of available acid combined at various times for equimolecular mixtures at 0° and at 20°. At 20°, the reaction is apparently complete when 75% of the acid has reacted. This is interpreted to mean that 50% of the propylene has reacted with 25% of the acid to form a chlorohexane, the remaining 50% of the propylene to form *iso*-

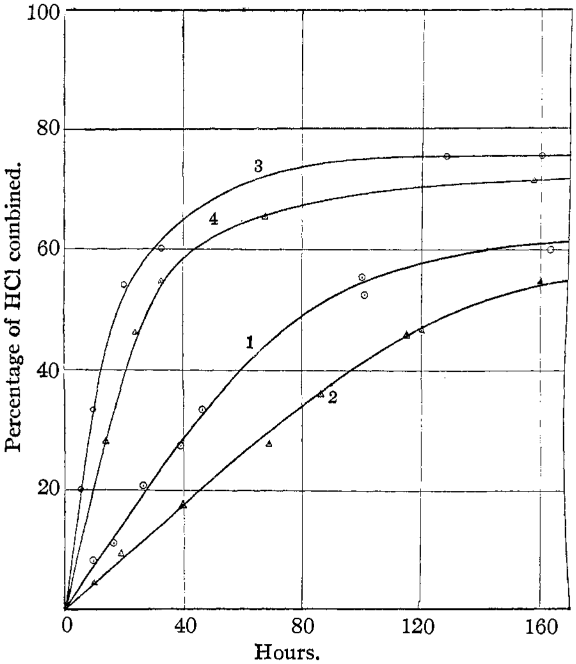

Fig. 1.—Curves 1 and 3, 20°; curves 2 and 4, 0°, abscissas of curves 3 and 4 reduced one-fifth.

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[7] Ref. 1, p. 2670.

[8] K. G. Falk, "Chemical Reactions," D. Van Nostrand Co., New York, **1920**, p. 137.

propyl chloride, which leaves 25% of the acid uncombined. At 20° the complete reaction yields a smaller quantity of chlorohexane.

One characteristic of all the reaction-velocity curves for the hydrogen bromide–propylene and hydrogen chloride–propylene reactions is the constancy of the rate of reaction at the beginning. For hydrogen chloride these rates are 0.016% per minute at 20° and 0.010% per minute at 0°, as compared to 2.04% per minute at 0° for the hydrogen bromide–propylene reaction.

Influence of Hydrogen Halide Concentration

Fig. 2 represents the reaction when there are two acid molecules to one of propylene. Apparently the concentration of the hydrogen chloride has a great influence on the rate, which is increased 14-fold. This is shown in another way. In a series of bulbs the reactants in various amounts were allowed to react for ten hours at 20°. The results are plotted in Fig. 3. The percentage of hydrogen chloride reacting is calculated on the basis of the reactant present in the smaller proportion. Similar experiments, in which the reaction times were half an hour, were carried out with hydrogen bromide at —78°. (See Fig. 3.)

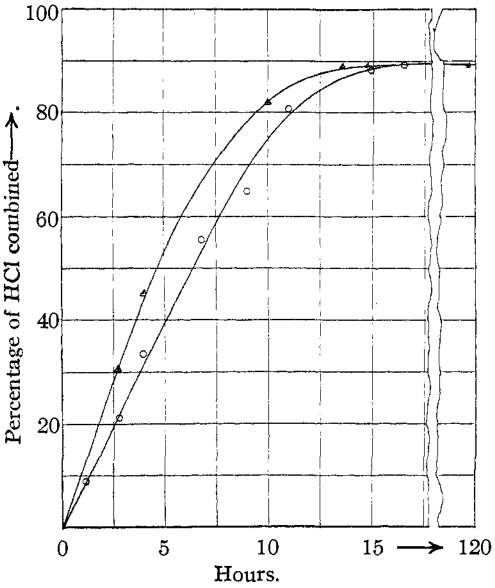

Fig. 2.—Upper curve, 20°; lower curve, 0°.

Furthermore, the following experiments were carried out. Two bulbs containing hydrogen chloride and propylene in the ratio 2:1 were kept for five days and nine days at —78.5°. The analysis showed that the rate of reaction was less than 1% in four hours. The hydrogen bromide-propylene reaction in an equimolecular mixture was found to have reacted 20% in this time (four hours) which is in agreement with the value found by Maass and Wright. But when hydrogen bromide, hydrogen chloride and propylene were mixed in equimolecular proportions, the reaction based on the amount of propylene present reached 82%. This experiment was repeated thrice, giving the same result, namely, a greatly increased rate of reaction. The connection between all of the concentration experiments described above and their interpretation will be considered in the discussion.

Reaction in the Gas Phase

Earlier experiments indicated that the reaction proceeds much more slowly, if at all, when the reactants are in the gaseous phase. An evacuated liter flask connected to a constant-level manometer was filled with a mixture of hydrogen chloride and propylene in the molecular ratio 2:1. A reaction would have been registered by a decrease in pressure. Observations carried out over a period of 400 days at room temperature showed that no perceptible reaction had occurred. A similar gaseous reaction mixture kept at a temperature of 100° for three days showed no evidence of reaction. In this latter case, however, the pressure measurements could not be made with equal accuracy on account of variation of temperature in the dead space.

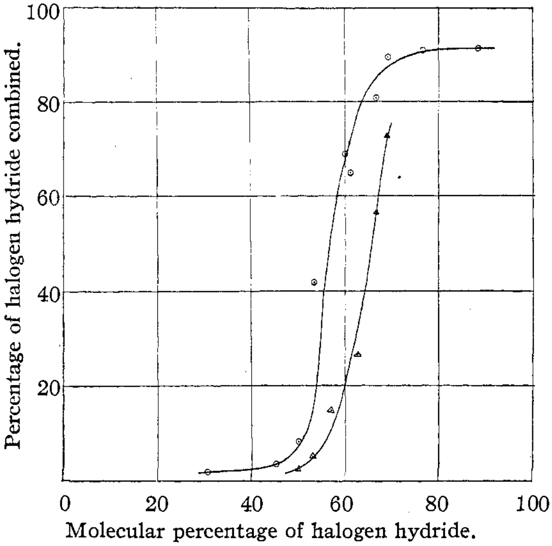

Fig. 3.—Upper curve; HCl, 20°, 10 hours. Lower curve; HBr, 78.5°, 0.5 hour.

Incidental Experiments

The reactants had always been dried with phosphorus pentoxide. It was of interest to determine the effect of water and of mercury upon the rate of the reaction in the liquid phase. Mercury was found to have no effect on the rate; 1 to 2% of water had only a slight effect. With large quantities of water two distinct liquid phases form and the velocity of the reaction is much increased.

It was also of importance to measure the conductivity of the reactant mixture to determine the presence or absence of ions. For this purpose a special cell capable of withstanding the high pressures exerted by the reactants was made. The results showed a complete absence of conduction.

Discussion of Results

Comparing the relative rates of reaction of the two halogen hydrides at the start, that of hydrogen bromide is seen to be 200 times as great as that of hydrogen chloride. In view of the hypothesis that the rate of reaction is dependent on molecular attraction, it follows that the molecular attraction between hydrogen bromide and propylene is greater than that between hydrogen chloride and propylene.

The reaction products of the hydrogen chloride reaction are *iso*propyl chloride (main reaction) and a chlorohexane, the latter being formed in a side reaction, that is, in smaller molecular quantity. The existence of these products was proved by analysis of the reaction mixture, and the formation of the chlorohexane gives an explanation of the apparently incomplete reaction when an equimolecular mixture is allowed to react and all the hydrogen chloride is not used up. It may be worth repeating that just as in the case of the hydrogen bromide reaction[7] it was proved that the hydrogen chloride reaction also is not a reversible equilibrium.

Change of temperature does not affect the main and side reactions to an equal extent, but rise in temperature favors the main reaction, as is clearly indicated by the larger amount of hydrogen chloride used up at 20° when an equimolecular mixture is allowed to react to completion.

The hydrogen chloride acts as a catalyst, excess of hydrogen chloride favoring the main reaction in a similar manner to a rise in temperature. The above data show, for instance, that at 0° in a mixture containing 2 molecules of hydrogen chloride to 1 of propylene, 80% of the available propylene forms *iso*propyl chloride and 20% the chlorohexane; whereas, at the same temperature in an equimolecular mixture, 50% of the propylene is used up in the main reaction and 50% in the side reaction.

That the effect of the excess halogen hydride is a catalytic one is shown by the experiments in which mixtures containing various molecular ratios were allowed to react over equal periods of time. The form of the curve is the same in the hydrogen chloride and in the hydrogen bromide reaction. A concentration effect would give a quite different curve from that found. The best evidence of the catalytic effect of the halogen hydride is given by the experiments in which mixtures of hydrogen bromide, hydrogen chloride and propylene in equimolecular proportions were allowed to react at —78°. At that temperature hydrogen chloride and propylene do not react to any measurable extent in an equimolecular mixture, therefore the hydrogen chloride might be looked upon as a diluent. Nevertheless, the rate of reaction was far greater than for a hydrogen bromide-propylene mixture of equimolecular proportions and nearly equal to that in which hydrogen bromide and propylene are mixed in a 2:1 ratio. In other words, the hydrogen chloride acted as a catalyst for the bromide reaction. It is improbable that the catalytic effect is due to ionic dissociation in view of the conductivity experiment described above, but it may be accounted for by the polar nature of the halogen hydride causing regional orientation in the liquid phase.[9]

Effect of Pressure and Temperature on Reaction Velocity

It was shown that no measurable reaction occurs between hydrogen chloride and propylene in the gaseous phase at a pressure of one atmosphere. Assume for the sake of argument that an experimental error equivalent to 0.2% unobserved reaction occurred in 400 days in the 2:1 mixture. If the gas has been compressed to have the same density as the liquid, a pressure of approximately 100 atmospheres would have been required. If the reaction is a bimolecular one, 20% $(100^{2-1}/5)$ would be the extent of the reaction in 400 days. But a 2:1 mixture in the liquid phase reacts to this extent inside of a few hours. Hence, the rate of the reaction is affected by pressure in some way quite other than by the influence of increased concentration. In our opinion with greater proximity of polar molecules regional orientation occurs favoring the formation of molecular complexes and enabling subsequent reaction to take place. This view may be made clearer by a consideration of our idea of the effect of temperature on the velocity of certain chemical reactions.

In the first place the reaction described is another example of one whose mechanism cannot be explained on the sole basis of the radiation theory of chemical reaction, since otherwise there would have been a reaction in the gaseous phase.

Consider a reaction to take place between two substances A and B to form a stable compound C, thus: $A + B \longrightarrow C$. The question to be discussed is: what factors govern the rate of formation of C?

For a clear understanding of what these factors are and how they may influence the reaction, it is desirable to consider separately the effects of the various forms of heat energy stored in the molecules, namely, translational, rotational and vibrational.

Translational Energy.—Considering the first of these: when Molecules A and B meet in collision they will remain together by virtue of their attraction for each other unless the translational energy stored up on impact is sufficient to hurl them back beyond the limits of this attraction. Therefore, the translational energy must be small and the attractive forces large in order that A and B may unite to form AB, which may be called a molecular compound or molecular complex.

Rotational Energy.—The attraction between the molecules A and B may be sufficiently large for them to remain together. It can only reach this maximum when they have a certain orientation with respect to each

[9] Taylor, "A Treatise on Physical Chemistry," D. Van Nostrand Co., New York, **1924**, p. 132.

other. But if they possess a high rotational energy, such orientation is hindered; therefore, rotational energy tends to inhibit, while, again attractive polar forces favor, the formation of the molecular compound AB.

Vibrational Energy.—Of the molecular complexes which are formed subject to the conditions just discussed, certain ones may have the capacity to react to form the stable compound C thus: $A + B \rightleftharpoons AB \longrightarrow C$. It is to be noted that there is an important difference between the formation of AB and of C. AB forms readily at very low temperatures because its formation means merely the satisfaction of existing residual valence. The formation of C, on the other hand, involves much greater energy changes, since the equilibrium of forces between atoms must be destroyed and primary valence bonds severed. This would result from a high vibrational energy which is, therefore, essential for the formation of C, once the molecular compound AB has formed. All the above can be expressed in terms of the effect of temperature and molecular attraction on the velocity of a chemical reaction. Translational, rotational and vibrational energies of the molecules are always in an energy equilibrium and each, therefore, is separately proportional to the temperature. A rise in temperature by increasing the first two will, therefore, hinder the reaction and by increasing the third will favor the reaction. The resultant effect of a change in temperature will, therefore, be difficult to predict. In any case the velocity of a chemical reaction will be greatly influenced by the value of the attraction of the reacting molecules for one another, because when this is great the relative effect of translational and rotational energy is lessened. Of two reactions compared at the same temperature, the one in which the molecules have the greater attraction for one another will proceed faster.

From this point of view the molecules which can react at any given time are given by that fraction calculated on the basis of Maxwell's distribution law whose velocities of translation lie below a certain value. The molecules in this fraction have various rotational velocities again distributed according to Maxwell's distribution law. The fraction of this fraction having values below a certain minimum can react. Finally, only a fraction of these will react, namely, those having a vibratory energy above a certain value.

This vibratory energy may have been obtained due to a previous collision or, in some cases, by the absorption of radiant energy or both. G. N. Lewis and D. F. Smith[10] have pointed out that the activated molecules may owe their internal energy both to collisional and radiation phenomena, and conclude that the number thus activated is far greater than that demanded by the reaction velocity. We suggest in the case of bimolecular reactions that this is due to the possibility that of this

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[10] Lewis and Smith, This Journal, **47**, 1508 (1925).

number only those having a certain minimum of rotational and translational energy can react.

In view of what has been said it may be clearer now that increased pressure causing closer proximity of molecules will tend to aid regional orientation and thus affect the velocity of the reaction. This may account for the difference in reaction rates in the liquid and gaseous states of the reaction investigated. It is the intention of the authors to investigate this reaction in the gaseous state at high pressures and over an extended temperature range with the hope of having further light thrown upon the above speculations.

Acknowledgment is hereby made of a bursary granted during the time of this research by the Honorary Council for Scientific and Industrial Research of Canada.

Summary

The velocity of reaction of propylene and hydrogen chloride in the liquid state was determined at 0° and 20° and compared to the analogous reaction involving hydrogen bromide.

The main product of the reaction was found to be *iso*propyl chloride. It was also shown that a side reaction involving the formation of a chlorohexane took place.

It was shown that the halogen hydride acts as a catalyst although no detectable ionization occurs.

No reaction was found to take place when hydrogen chloride and propylene were mixed in the gaseous state at low pressures.

The idea was advanced that the various forms of thermal energy influence the rate of a chemical reaction in different ways. The kinetic energy of rotation and translation of the molecules actually hinders chemical combination, whereas the vibrational energy furthers it. This presents a new view of the influence of temperature and pressure on the velocity of the chemical reaction.

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