[CONTRIBUTION FROM THE RICHARD B. WETHERILL LABORATORY OF PURDUE UNIVERSITY]

# Kinetics, Relative Rate and Partial Rate Factors for the Gallium Bromide-catalyzed Reaction of Isopropyl Bromide with Toluene and Benzene[1]

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An experimental technique, utilizing high vacuum methods, has been developed for following the rates of alkylation of aromatic hydrocarbons in Friedel–Crafts reactions. The new method, based upon the measurement of the pressure of hydrogen halide liberated in the reaction, is applicable to the determination of the rates of relatively fast reactions requiring study at low temperatures. With the aid of this procedure, the rate of reaction of isopropyl bromide with toluene, under the catalytic influence of gallium bromide, was determined. The results reveal that the reaction follows pseudo zero-order kinetics, identical with the order observed previously for the corresponding reactions of methyl and ethyl bromide. The second-order rate constant for the reaction was 0.350, 1.46 and 8.00 l. mole$^{-1}$ sec.$^{-1}$ at $-78.5$, $-63.7$ and $-45.3°$, respectively. At 25° the relative rates of reaction of methyl, ethyl and isopropyl bromides with toluene are 1.00, 13.7 and 20,000, respectively. The energy of activation and log $A$ terms are 8.3 kcal. mole$^{-1}$ and 8.9 (sec.$^{-1}$). The values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are 7.9 kcal. mole$^{-1}$ and $-19.3$ e.u. The toluene/benzene reactivity ratio, $k_T/k_B$, was determined to be 1.82 at 25° by competitive reaction. This relative rate was combined with the isomer distribution in the toluene reaction to calculate the partial rate factors: $o_f$ 1.52; $m_f$ 1.41; $p_f$ 5.05.

In the course of our studies of the kinetics and mechanism of the Friedel–Crafts reaction, we observed that gallium bromide was an effective, but mild catalyst[4] which avoided undesirable side-reactions, such as isomerization and disproportionation, characteristic of aluminum bromide catalysis.[5] The kinetics of the gallium bromide-catalyzed reactions of methyl and ethyl bromide with benzene and toluene, in the presence of a large excess of the aromatic as the reaction medium, was studied.[4] The reactions followed pseudo zero-order kinetics; they were zero order in the alkyl bromide and second order in the catalyst, gallium bromide. The reactions were presumably first order in the aromatic utilized as the reaction medium. However, this point could not be tested kinetically. The rate data were combined with the observed isomer distributions to calculate partial rate factors for the two substitution reactions.[6]

The corresponding reaction of isopropyl bromide proved to be very fast, with a half-life of approximately 0.01 sec. indicated by some rough flow experiments. A precise knowledge of the rate and of the entropy of activation for the reaction appeared highly important to the proper interpretation of the reaction mechanism. Accordingly, we undertook to develop an experimental technique which would permit us to observe the kinetics of the reaction, to measure the rates at several temperatures, and thereby attain a knowledge of the entropy of activation. Having achieved success in this endeavor, with toluene as the aromatic, we determined the toluene/benzene rate ratio competitively, and combined the results with the isomer distribution[6] to calculate the partial rate factors.

## Results

**The Kinetic Technique.**—The method adopted for following the kinetics was the measurement of the pressure of hydrogen bromide developed above a dilute solution of alkyl bromide and gallium bromide in toluene at low temperatures.

$$RBr + C_6H_5CH_3 \xrightarrow{GaBr_3} RC_6H_4CH_3 + HBr$$

Hydrogen bromide and gallium bromide interact with the aromatic hydrocarbon to form $\sigma$-complexes.[7] Fortunately, these complexes are much less stable than the corresponding derivatives of aluminum bromide.[8] By utilizing dilute solutions of gallium bromide and by limiting the kinetic observations to the initial stages of the reactions, it proved possible to circumvent the difficulty.

The rates of reaction of methyl and ethyl bromides with toluene, under the influence of gallium bromide, had previously been determined at 15.0, 25.0, and 40.0°, utilizing standard analytical procedure for following the course of the reaction. In order to test the validity of the present technique, we determined the rate of reaction of methyl bromide with toluene at 0°, and the rates of reaction of ethyl bromide with toluene at 0 and $-23.2°$. The linearity of the log $k_2$ *vs.* $1/T$ plots were examined to test the validity of the new experimental procedure.

In the gallium bromide-catalyzed reaction of methyl bromide with toluene at 0°, the pressure of hydrogen bromide increased linearly with time in the initial phases of the reaction, corresponding to the pseudo zero-order reaction observed previously at the higher temperatures. The zero-order rate constant for this reaction, $k_0$, was calculated from the data to be $2.55 \times 10^{-6}$ mole l.$^{-1}$ sec.$^{-1}$. The second-order rate constant was then obtained by dividing the value of $k_0$ by the square of the catalyst concentration, 0.0303 $M$ (as $GaBr_3$). Therefore the second-order rate constant is $0.278 \times 10^{-2}$ l. mole$^{-1}$ sec.$^{-1}$.

The high volatility of methyl bromide introduces experimental difficulties, both in the kinetic experiments utilizing the earlier procedures at higher temperatures and in the present experiments at 0°. Unfortunately, the slowness of the reaction prevents running the reaction at still lower tempera-

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[1] The Catalytic Halides. XXVI. Directive Effects in Aromatic Substitution. XXXIV.

[2] Post-doctorate research associate, 1956–1957, on project no. AT(11-1)-170 supported by the Atomic Energy Commission.

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[4] C. R. Smoot and H. C. Brown, THIS JOURNAL, **78**, 6245, 6249 (1956).

[5] H. C. Brown and H. Jungk, *ibid.*, **77**, 5579 (1955); H. C. Brown and C. R. Smoot, *ibid.*, **78**, 2176 (1956).

[6] H. C. Brown and C. R. Smoot, *ibid.*, **78**, 6255 (1956).

[7] S. U. Choi, Ph.D. thesis, Purdue University Library.

[8] H. C. Brown and W. J. Wallace, THIS JOURNAL, **75**, 6268 (1953).

tures which might minimize the uncertainties arising from this cause. In view of these difficulties, the agreement in the rate constant measured at 0° by the present method with the values obtained at higher temperatures by the earlier method must be considered reasonable.

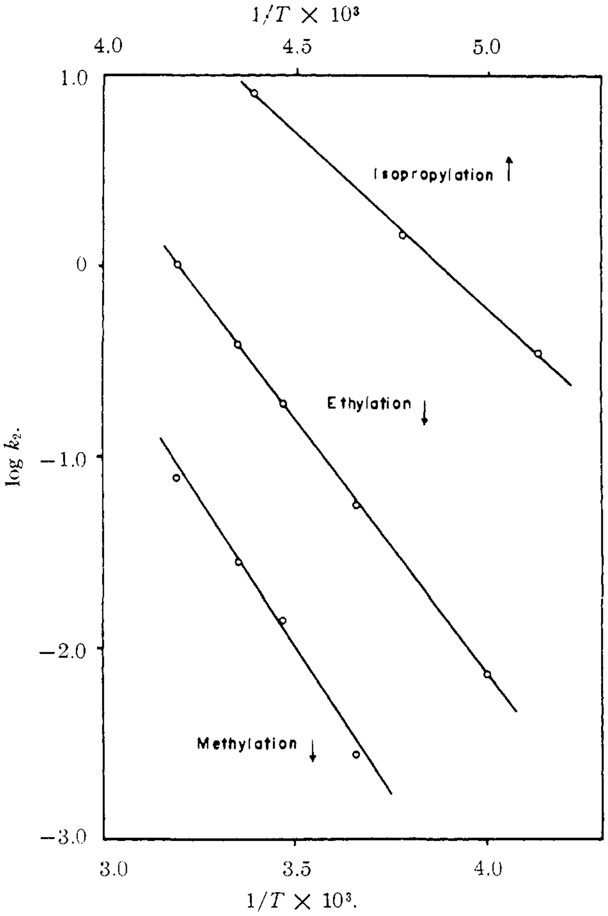

Fig. 1.—Temperature variation in the second-order rate constants for the reaction of toluene with methyl, ethyl and isopropyl bromide under the influence of gallium bromide.

The higher reactivity and lower volatility of ethyl bromide permitted a more rigorous test. In this case the rate constants at 0.0 and −23.2°, determined by the present procedure, are in excellent agreement with the earlier values at elevated temperatures (Fig. 1). The rate constants are summarized in Table I.

Table I

Rate Constants for the Gallium Bromide-catalyzed Reactions of Methyl and Ethyl Bromide with Toluene in Excess Toluene as Solvent

| Temp., °C. | Reactants, $M$ [MeBr] | [EtBr] | [GaBr$_3$] | Rate constants[a] $k_0 \times 10^5$, mole l.$^{-1}$ sec.$^{-1}$ | $k_2 \times 10^2$, l. mole$^{-1}$ sec.$^{-1}$ |
|---|---|---|---|---|---|
| −23.2 | | 0.422 | 0.0311 | 0.72 | 0.747 |
| 0.0 | 0.300 | | .0303 | | .278 |
| .0 | | .903 | .0392 | 8.22 | 5.35 |
| .0 | | .485 | .0323 | 5.95 | 5.70 |
| .0 | | .304 | .0103 | 0.64 | 6.05 |
| | | | | Av. | 5.70 |

[a] Methyl bromide, $k_2 \times 10^2$ l. mole$^{-1}$ sec.$^{-1}$: 15.0°, 1.43; 25.0°, 2.85; 40°, 7.67. Ethyl bromide, $k_2 \times 10^2$ l. mole$^{-1}$ sec.$^{-1}$: 15.0°, 19.1; 25.0°, 39.2; 40.0°, 102 (ref. 4).

In view of the agreement realized, it was considered that the experimental technique was capable of giving rate data of the desired precision.

**Isopropylation of Toluene.**—Utilizing the present method of kinetic study, the gallium bromide-catalyzed reaction of isopropyl bromide with toluene, in the latter as reaction medium, was investigated at −78.5, −63.7 and −45.3°. Typical data are shown graphically in Fig. 2. Since the plots of the pressure in the system *versus* time exhibit good linearity, it was concluded that the reaction follows pseudo zero-order kinetics in toluene, just as in the case of the methyl and ethyl bromides.

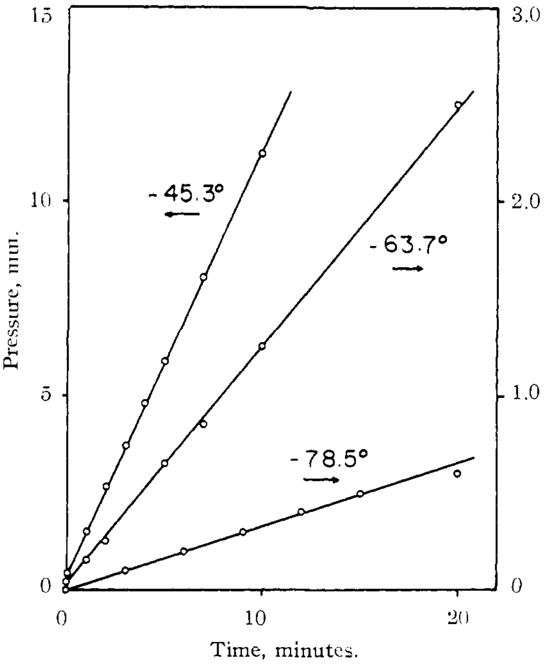

Fig. 2.—Increase of pressure with time in the gallium bromide-catalyzed reaction of toluene with isopropyl bromide.

Variation of the initial concentration of isopropyl bromide did not alter the observed rate constant. However, the zero-order rate constants are influenced by the initial concentration of the catalyst. Values of $k_1$, obtained by dividing $k_0$ by the initial concentration of gallium bromide, were not constant. However, values of $k_2$, obtained by dividing $k_0$ by the square of the catalyst concentration, did exhibit satisfactory constancy. Consequently, the kinetics exhibited by isopropyl bromide in this reaction are identical with those observed previously for methyl and ethyl bromides.[4]

The rate constants are summarized in Table II. The variation in the second-order rate constant with temperature is illustrated in Fig. 1.

**Relative Rate of Isopropylation of Toluene and Benzene.**—Because of the high melting point of benzene, it was impossible to measure directly its rate of isopropylation. Accordingly, we undertook to measure the toluene/benzene reactivity ratio, $k_T/k_B$, in this reaction competitively. A mixture of benzene and toluene was allowed to

TABLE II

RATE CONSTANTS FOR THE GALLIUM BROMIDE-CATALYZED REACTION OF ISOPROPYL BROMIDE WITH TOLUENE IN EXCESS TOLUENE AS SOLVENT

| Temp., °C. | Reactants, $M$ [$i$-PrBr] | Reactants, $M$ [GaBr$_3$] | Rate constants $k_0 \times 10^4$, mole l.$^{-1}$ sec.$^{-1}$ | Rate constants $k_1 \times 10^2$, sec.$^{-1}$ | Rate constants $k_2$, l. mole$^{-1}$ sec.$^{-1}$ |
|---|---|---|---|---|---|
| −63.7 | 0.347 | 0.0293 | 12.7 | 4.35 | 1.48 |
| | .352 | .0175 | 3.98 | 2.28 | 1.30 |
| | .304 | .0144 | 3.20 | 2.22 | 1.54 |
| | .397 | .00733 | 0.812 | 1.11 | 1.51 |
| | .669 | .00511 | .422 | 0.825 | 1.61 |
| | .361 | .00352 | .163 | .462 | 1.31 |
| | | | | Av. | 1.46 |
| −78.5 | .585 | .0137 | .608 | | 0.323 |
| | .586 | .0112 | .475 | | .378 |
| | | | | Av. | .350 |
| −45.3 | .306 | .0139 | 15.5 | | 8.05 |
| | .280 | .00788 | 5.32 | | 8.56 |
| | .475 | .00627 | 2.93 | | 7.38 |
| | | | | Av. | 8.00 |

react with isopropyl bromide at 25° under the influence of gallium bromide. After a very short reaction time, 30 seconds, the reaction mixture was analyzed by fractionation. From these results, the toluene/benzene reactivity was calculated with the aid of the usual expression

$$\frac{k_T}{k_B} = \frac{\log[b] - \log[b - y]}{\log[a] - \log[a - x]}$$

where $a$ and $b$ are the numbers of moles of benzene and toluene initially present in the mixture and $x$ and $y$ are the moles of isopropylbenzene and isopropyltoluene formed in the reaction mixture.[9] The data indicate a $k_T/k_B$ value of 1.82.

The results are summarized in Table III.

TABLE III

TOLUENE/BENZENE REACTIVITY RATIO FOR THE GALLIUM BROMIDE-CATALYZED REACTION WITH ISOPROPYL BROMIDE AT 25.0°

| | Detn. 1 | Detn. 2 |
|---|---|---|
| Reactants[a] | | |
| Benzene | 234 | 211 |
| Toluene | 238 | 214 |
| Isopropyl bromide | 61.2 | 55.1 |
| GaBr$_3$ | 2.53 | 2.16 |
| Products[a] | | |
| Benzene | 219 | 199 |
| Toluene | 212 | 191 |
| Isopropyl bromide | 30.7 | 33.1 |
| Isopropylbenzene | 7.5 | 6.0 |
| Isopropyltoluene | 14.3 | 10.4 |
| Reactivity ratio, $k_T/k_B$ | 1.91[b] | 1.73[b] |

[a] Mmoles. [b] Av. 1.82.

## Discussion

The rate constants observed for the gallium bromide-catalyzed alkylation reaction are summarized in Table IV.

TABLE IV

RATE CONSTANTS FOR THE GALLIUM BROMIDE-CATALYZED REACTION OF ALKYL BROMIDES WITH BENZENE AND TOLUENE IN EXCESS AROMATIC AS SOLVENT

| Alkyl bromide | Temp., °C. | Benzene Rate constant $k_2 \times 10^2$, l. mole$^{-1}$ sec.$^{-1}$ | Benzene Rel. rate, RBr/MeBr | Toluene Rate constant $k_2 \times 10^2$, l. mole$^{-1}$ sec.$^{-1}$ | Toluene Rel. rate, RBr/MeBr |
|---|---|---|---|---|---|
| Methyl | 0.0 | | | 0.278 | |
| | 15.0 | 0.228 | | 1.43[c] | |
| | 25.0 | 0.500 | 1.00 | 2.85[c] | 1.00 |
| | 40.0 | 1.31 | | 7.67[c] | |
| Ethyl | −23.2 | | | 0.747 | |
| | 0.0 | | | 5.70 | |
| | 15.0 | 7.53 | | 19.1[c] | |
| | 25.0 | 15.9 | 32 | 39.2[c] | 13.7 |
| | 40.0 | 42.5 | | 102[c] | |
| Isopropyl | −78.5 | | | 35.0 | |
| | −63.7 | | | 146 | |
| | −45.3 | | | 800 | |
| | 25.0 | 32000[a] | 64000 | 58000[b] | 20000 |

[a] Calculated from the $k_T/k_B$ rate ratio of 1.82. [b] Calculated from the rate constants at lower temperatures. [c] Ref. 4.

Previously we had attempted to arrive at an estimate of the rate constant for the reaction of toluene and isopropyl bromide by utilizing a flow reactor with a contact time of approximately 0.005 sec. The rate constant estimated by that procedure is larger than the present value by approximately a factor of 10.[4] In the flow reactor no provision was present to permit control of the temperature in the fine capillary through which the reacting materials passed. Possibly the temperature in this capillary was significantly higher than the external temperature.[10]

The rate of reaction of methyl, ethyl and isopropyl bromides with toluene increases markedly with the branching of the alkyl bromide: methyl, 1.00; ethyl, 13.7; isopropyl, 20,000. The mechanism of the reaction of benzene and toluene with methyl and ethyl bromides had been previously discussed.[4] It was pointed out that the ability of the alkyl group to accommodate a positive charge was evidently quite important, but that the ability of the aromatic to form a bond was also important. Consequently, the reaction must involve a reaction of the aromatic with a more or less polarized alkyl bromide–gallium bromide complex. It was considered that the observed entropies of activation of −20 e.u. supported the proposed mechanism.

The large increase in the rate for isopropyl bromide suggested the possibility of a change to a predominantly ionization mechanism. Such a change in mechanism should be accompanied by a marked change in the entropy of activation. The hope of testing this question was one of the major objectives of the present study.

In the case of methyl and ethyl bromides we have utilized all of the available rate constants (Table IV) for a least squares calculation of the reaction values. The values for isopropyl bromide are based on the rate constants observed in the present study. The calculated values of the constants of the Arrhenius expression and the energies and entropies of activation are summarized in Table V.

It is clear from the constancy of the values for the entropy of activation that the results do not sup-

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(9) This equation is based on the assumption that the reaction is first order in the aromatic. See discussion in the Experiment Part.

(10) In view of this discrepancy, the corresponding rate for the reaction of $t$-butyl bromide with toluene must also be considered circumspect.

TABLE V

ENERGIES AND ENTROPIES OF ACTIVATION FOR THE GALLIUM BROMIDE-CATALYZED REACTION OF ALKYL BROMIDES WITH TOLUENE

| Alkyl bromide | $E_{ac}$ | log $A$, sec.$^{-1}$ | $\Delta H^{\ddagger}$ | $\Delta S^{\ddagger}$ |
|---|---|---|---|---|
| Methyl | 14.0 | 8.71 | 13.4 | −20.0 |
| Ethyl | 12.1 | 8.49 | 11.6 | −21.5 |
| Isopropyl | 8.3 | 8.86 | 7.9 | −19.3 |

port the suggested change in reaction mechanism. From the constancy we must conclude that there is no significant change in the reaction mechanism in this series of alkyl bromides.

The observed data indicate that the ability of the alkyl group to tolerate a positive charge must contribute in an important way to the stability of the transition state. Likewise the bond-making ability of the aromatic must also contribute to the formation of the activated complex. The change in rate with structure of the alkyl group is far larger than the change in rate with variation of the aromatic. Consequently, the breaking of the carbon–bromine bond must be considered to contribute in a more important way to the stability of the transition state than the bond making by the aromatic.

In the case of methyl bromide, the $k_T/k_B$ ratio at 25.0° is 5.7. The corresponding ratio for ethyl bromide is 2.5, and it drops to 1.82 for isopropyl bromide. Consequently, it appears that bond-making by the aromatic is greatest with methyl bromide and decreases with the increasing ability of the alkyl group to accommodate a positive charge.

Utilizing the isomer distribution at 25.0°[6] and the relative rate data of the present study, we can calculate the partial rate factors. These are summarized in Table VI.

TABLE VI

PARTIAL RATE FACTORS AND SELECTIVITY FACTORS FOR THE GALLIUM BROMIDE-CATALYZED ALKYLATION OF TOLUENE

| Reaction | Partial rate factors | | | |
|---|---|---|---|---|
| | $o_f$ | $m_f$ | $p_f$ | $S_f$ |
| Methylation[a] | 9.51 | 1.70 | 11.8 | 0.842 |
| Ethylation[a] | 2.84 | 1.56 | 6.02 | .587 |
| Isopropylation | 1.52 | 1.41 | 5.05 | .554 |

[a] Ref. 6.

The partial rate factors provide an excellent fit with the Selectivity Relationship.[11]

## Experimental Part

**Materials.**—The purification of toluene, benzene and gallium bromide were described in previous papers in this series.[4] Methyl bromide (Matheson) was withdrawn from the cylinder, introduced into the vacuum line, and fractionated. Material of tensiometric homogeneity, v.p. 663.5 mm. at 0°, was utilized. Ethyl bromide was dried over calcium hydride, distilled in a column of 52 theoretical plates, b.p. 38.0° at 745 mm., $n^{20}D$ 1.4241. It was introduced into the vacuum line and material of tensiometric homogeneity, v.p. 165.2 mm. at 0°, was utilized in the rate experiments. Isopropyl bromide was purified in the same manner: b.p. 60.0°, $n^{20}D$ 1.4251; v.p. 69.15 mm. at 0°, 4.30 mm. at −45.3°, 1.00 mm. at −63.7° and 0.25 mm. at −78.5°.

**Apparatus for the Kinetic Measurements.**—All of the kinetic experiments were carried out by high vacuum techniques.[12] The apparatus used for the kinetic measurements is shown diagramatically in Fig. 3.

**Procedure for the Kinetic Measurements.**—A solution of gallium bromide in toluene of known concentration was prepared in thin-walled glass bulbs under vacuum in the following manner. After the apparatus in Fig. 4 was degassed, a known quantity of gallium bromide was sublimed into tube A by the technique described earlier.[4,7] The side tube B was sealed off at the constriction C under vacuum. A known amount of toluene was then transferred from the weighing tube (not shown in Fig. 4) to the tube A by the usual vacuum line techniques. The entire apparatus was then sealed off at the constriction E and separated from the vacuum line. After all of the gallium bromide had dissolved in toluene at room temperature, the entire apparatus was tilted so that the solution could flow down to the buret section where the total volume of the solution was measured. The apparatus was then tilted, so that a portion of the solution flowed into the first thin-walled bulb $G_1$, which was then sealed off from the apparatus and sealed to a glass-enclosed iron core H. The volume of the remaining solution was measured after it was brought back to the buret by tilting. In this way, each of the bulbs were filled in turn with known volumes of a standard solution of gallium bromide in toluene, without exposure to air.

One of these bulbs thus prepared was placed in the reaction vessel together with a glass-enclosed stirring bar. The reaction vessel was then connected to the high vacuum apparatus, as shown in Fig. 3. After the reaction vessel was evacuated, a known amount of toluene was transferred from the weighing tube to the reaction vessel, followed by a known quantity of the alkyl bromide. (Methyl bromide was measured as a gas; ethyl and isopropyl bromide were transferred from weighing tubes.) The reaction vessel was immersed in a bath at the desired temperature and the magnetic stirrer was put into place. After sufficient time to achieve temperature equilibrium, the magnetic stirrer was started and the reaction was started by dropping and breaking the bulb. This moment was taken as zero time. The pressure was determined on the manometer at measured intervals of time. The cold baths were prepared from solid–liquid mixtures: ice, 0°; carbon tetrachloride, −23.2°; chlorobenzene, −45.3°; chloroform, −63.7°; solid carbon dioxide in trichloroethylene, −78.5°.

In the calculation of the initial concentrations of gallium bromide and alkyl bromides, the volume of the liquid phase should be known. It was assumed to be the sum of the volume of alkyl bromides and toluene, utilizing the following densities: toluene,[13] 0.884 at 0°, 0.906 at −23.2°, 0.927 at −45.3°, 0.944 at −63.7° and 0.959 at −78.5°; methyl bromide,[14] 1.732 at 0°; ethyl bromide,[15] 1.501 at 0° and 1.550 at −23.2°; isopropyl bromide,[16] 1.370 at −45.3°, 1.397 at −63.7° and 1.420 at −78.5°.

**The Kinetic Method.**—The basis of this procedure is the measurement of the partial pressure of hydrogen bromide above the reaction mixture. Assuming that hydrogen bromide obeys the ideal gas law under the conditions of the experiments and that the room temperature remains constant during each run of the experiment, it follows that the number of moles, $n'$, of hydrogen bromide present in the vapor phase is proportional to its partial pressure, $p$, over the reaction mixture.[17]

$$n' = a_1 p \tag{1}$$

The partial pressure of hydrogen bromide is also proportional

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(11) See Fig. 1 in H. C. Brown and G. Marino, THIS JOURNAL, **81**, 3308 (1959), for a graphical representation of the agreement.

(12) R. T. Sanderson, "Vacuum Manipulation of Volatile Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948.

(13) "International Critical Tables," McGraw–Hill Book Co., Inc., New York, N. Y., 1928.

(14) N. A. Lange, "Handbook of Chemistry," 8th Editiion, Handbook Publishers, Inc., Sandusky, Ohio, 1952.

(15) J. Timmermans, "Physico-Chemical Constants of Pure Organic Compounds," Elsevier Publishing Co., Inc., New York, N. Y., 1950.

(16) Present study.

(17) The constant $a_1$ may be evaluated from the relationship, $a_1 = V/RT$, where $R$ is the gas constant, $T$ is the room temperature (°K.), and $V$ is the apparent volume of the vapor phase of the system, obtained by subtracting the volume of the liquid phase from the apparent volume of the reaction vessel measured after the completion of each kinetic run. The apparent volume is measured by measuring the pressure exerted by a known amount of gas with the reaction vessel immersed in the constant temperature-bath to an etched reference line.

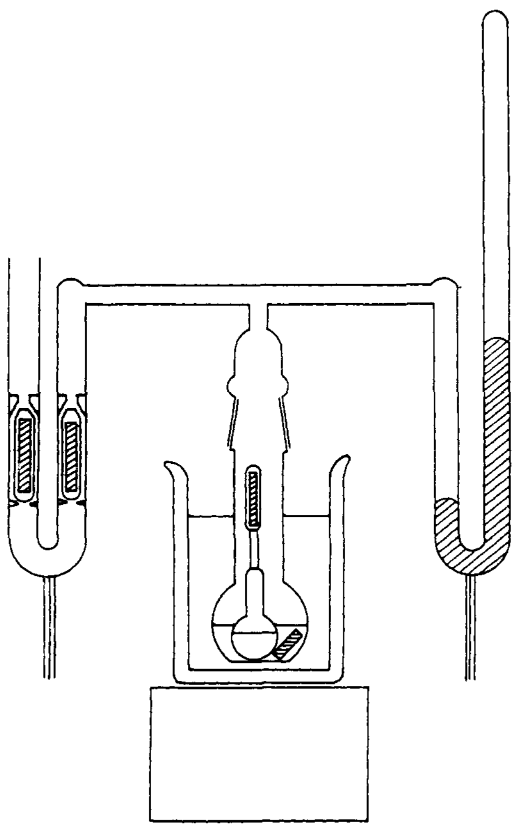

Fig. 3.—Apparatus used for the kinetic studies.

to its mole fraction in the liquid phase of the system (Henry's law). Since a large excess of aromatic is used as the reaction medium, the total number of moles of the reaction mixture can be assumed to remain constant throughout each experiment. Therefore, the number of moles, $n''$, of hydrogen bromide present in the liquid phase of the system is proportional to its partial pressure above the reaction mixture

$$n'' = a_2p \qquad (2)$$

By combining the equations 1 and 2, it can be said that the total number of moles, $n$, of hydrogen bromide present in the entire system (both liquid and vapor phases) is proportional to its partial pressure over the reaction mixture

$$n = ap \qquad (3)$$

The rate of reaction is, therefore, expressed by the equation

$$\text{rate} = \frac{\mathrm{d[HBr]}}{\mathrm{d}t} = \frac{\mathrm{d}(n/V_1)}{\mathrm{d}t} = \frac{a}{V_1}\frac{\mathrm{d}p}{\mathrm{d}t} \qquad (4)$$

where $V_1$ is the volume of the liquid phase of the system. Thus the rate can be measured by following the partial pressure of hydrogen bromide over the reaction mixture, evaluating the constant $a$ in the following manner. After completion of the reaction

$$n_\infty = ap_\infty$$

where the subscript $\infty$ denotes the corresponding quantities of hydrogen bromide after the completion of the reaction. If there is no side reaction, the value of $n_\infty$ should be identical to the number of moles, $n^\circ_{\mathrm{RBr}}$, of the alkyl bromide originally introduced into the system. It follows that the rate of the reaction is given by the expression

$$\text{rate} = \frac{n^\circ_{\mathrm{RBr}}}{V_1p_\infty}\frac{\mathrm{d}p}{\mathrm{d}t} \qquad (5)$$

For reactions of zero order, as observed in the present study, equation 5 can be simplified further, since the pressure varies linearly with time

$$\mathrm{d}p/\mathrm{d}t = p_\infty/t_\infty \qquad (6)$$

where $t_\infty$ is the time required for the completion of the reaction. Therefore, the zero-order rate constant, $k_0$, can be calculated from equation 7 by determining the value of $t_\infty$

$$k_0 = n^\circ_{\mathrm{RBr}}/V_1t_\infty \qquad (7)$$

The value of $t_\infty$ is conveniently obtained by extrapolating the initial, linear portion of the plots of the total pressure of the system *vs.* time to the corresponding pressure measured after the completion of the reaction.[18]

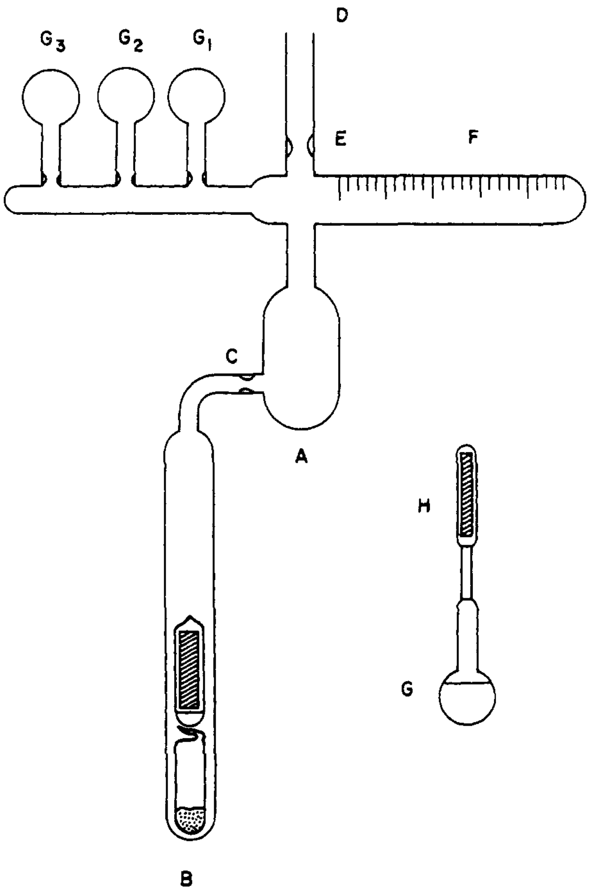

Fig. 4.—Apparatus used to prepare solutions of gallium bromide in toluene.

Several assumptions were made in arriving at the rate expression 7 and in proceeding from this rate expression to the rate constants. However, any errors arising from this treatment appear to be no greater than the experimental error. This conclusion is supported by the following arguments. First, the kinetics of the gallium bromide-catalyzed reaction of ethyl bromide with benzene in 1,2,4-trichlorobenzene have been studied both by the present experimental technique in a vacuum system and by the standard method of titrimetric analysis of hydrogen bromide.[4] The rate constants by both methods agree to within the usual experimental error.[19] Second, the values of the rate constants for the gallium bromide-catalyzed reactions of methyl and ethyl bromides with toluene at lower temperatures, determined by the present pressure technique, agree closely (Table I, Fig. 1) with the rate constants determined at higher temperatures by standard kinetic methods.[4] Finally,

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[18] Initially the pressures increased linearly with time (Fig. 2). However, this was followed by a decrease in rate, which appeared to be greater than any reasonable reaction order would predict. We attributed this decrease to the removal of catalyst through the formation of $\sigma$-complexes with hydrogen bromide and aromatic. Consequently, the rate constants were based upon the initial, linear portion of the reaction.

[19] Unpublished data of S. U. Choi.

the values of $p_\infty$ calculated from equations 8 are consistent with the observed experimental values (Table VII).

$$n'_\infty = a_1 p_\infty$$
$$n''_\infty = a_2 p_\infty \qquad (8)$$
$$n'_\infty/a_1 = n''_\infty/a_2$$

TABLE VII

PARTIAL PRESSURE OF HYDROGEN BROMIDE OVER THE REACTION MIXTURE AFTER THE COMPLETION OF THE ALKYLATION REACTIONS OF TOLUENE

| Alkyl bromide | MeBr | EtBr | EtBr |
|---|---|---|---|
| Temp., °C. | 0.0 | 0.0 | −23.2 |
| Apparent vol., cc. | 43.2 | 46.5 | 48.8 |
| Rm. temp., °C. | 23.1 | 25.2 | 24.5 |
| Henry's law const., mm. | 4230 | 4250 | 1970 |
| Toluene, mmoles | 75.269 | 43.050 | 45.773 |
| Alkyl bromide, mmoles | 2.391 | 4.334 | 2.053 |
| $Ga_2Br_6$, mmole | 0.121 | 0.094 | 0.075 |
| $p_\infty$, calcd., mm. | 116 | 317 | 76.1 |
| $p_\infty$, obsd., mm.[a] | 117.0 | 313.2 | 77.6 |

[a] The values of $p_\infty$, obsd., are obtained by subtracting the vapor pressure of the aromatic at the temperature investigated (6.70 mm. at 0° and 1.20 mm. at −23.2°) from the total pressure of the system measured after the completion of the reaction.

The value of $a_1$ can be calculated from the values of the apparent volume of the vapor phase of the system and the room temperature. The value of $a_2$ can also be calculated from the values of the total number of the moles of reactants introduced and the Henry's law constant for hydrogen bromide over the reaction mixture determined experimentally after the completion of the reaction by removing all the hydrogen bromide liberated by the reaction from the reaction mixture and by measuring the solubility of hydrogen bromide in the mixture of the reaction products. The above equation can then be solved for $n'_\infty$, since $n''_\infty = n^\circ_{RBr} - n'_\infty$. Therefore, the values of $p_\infty$ are calculated from equation 8.

Typical rate data are summarized in Table VIII.

TABLE VIII

RATE DATA FOR GALLIUM BROMIDE-CATALYZED REACTION OF ISOPROPYL BROMIDE WITH TOLUENE AT −45.3°

| Time, min. | Press., mm. Run 1 | Run 2 | Run 3 |
|---|---|---|---|
| 0 | 0.40 | 0.35 | 0.40 |
| 0.5 | 3.40 | . . | . . |
| 1 | 6.40 | 2.65 | 1.50 |
| 2 | 10.40 | 5.00 | 2.65 |
| 3 | 11.85 | 7.25 | 3.70 |
| 4 | . . . | 9.30 | 4.80 |
| 5 | 14.00 | 10.70 | 5.90 |
| 7 | . . . | 12.40 | 8.05 |
| 10 | . . . | 13.65 | 11.20 |
| 15 | . . . | . . . | 15.15 |
| ∞ | 20.10 | 20.55 | 29.95 |
| ArH, mmoles | 61.63 | 84.71 | 39.97 |
| RBr, mmoles | 1.929 | 2.423 | 1.970 |
| $GaBr_3$, mmole | 0.0876 | 0.0681 | 0.0260 |
| $t_\infty$, min.[a] | 3.28 | 8.78 | 26.9 |
| $V_1$, ArH, cc. | 6.125 | 8.419 | 3.972 |
| $V_1$, RBr, cc. | 0.173 | 0.218 | 0.177 |

[a] Run 1: $p_{obs} = 6.00t + 0.40$; 2: $p_{obs} = 2.30t + 0.35$; 3: $p_{obs} = 1.10t + 0.40$.

**Relative Rate of Reaction, Toluene/Benzene.**—A known quantity of gallium bromide was introduced into an empty storage tube in the vacuum line, and a known amount of toluene transferred into the tube. Dry nitrogen was introduced and the tube was sealed off and removed from the vacuum apparatus. The tube was then tilted in such a way that the solution flowed down into a thin-walled bulb which had been sealed previously to the tube. The thin bulb was sealed off at the constriction and placed in a 100-ml. round-bottom flask containing carefully measured quantities of benzene, toluene and isopropyl bromide. The reaction was started by breaking the fragile bulb containing the catalyst solution. After 30 seconds, the reaction mixture was quenched by pouring into ice-water. The organic layer was washed with bicarbonate solution, washed with water, and dried over Drierite. The reaction mixture of benzene, toluene, isopropylbenzene and isopropyltoluenes was analyzed by fractionation in a Podbielniak Micro Analyzer, using tetralin as the chaser. The results are summarized in Table III.

In this study the order with respect to the aromatic solvent could not be determined. We have assumed that the reaction is first order in solvent and utilized the usual equation employed for such reactions to calculate the reactivity ratio. Actually, the assumption that the reaction is first order in aromatic is not essential. If it is assumed that the order with respect to benzene and toluene is the same, it is possible to calculate the relative rate, using the expression $k_T/k_B = y/x$, providing that there is present in the reaction mixture the same number of moles of benzene and toluene. In these competitive experiments, the number of moles of the two aromatics was maintained sensibly equal. Use of this alternative equation yields the same value of $k_T/k_B$.

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[CONTRIBUTION FROM THE RICHARD B. WETHERILL LABORATORY OF PURDUE UNIVERSITY]

# Relative Rate and Isomer Distribution in the Gallium Bromide-catalyzed Benzylation of Benzene and Toluene[1]

BY HERBERT C. BROWN AND BRIAN A. BOLTO[2]

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Under the influence of gallium bromide, benzyl bromide undergoes an exceedingly rapid reaction with benzene and toluene. Attempts to measure the individual reaction rates failed. Utilizing a competitive method, the relative rate of benzylation of toluene and benzene at 25° was established as 4.0. The isomer distribution in the benzylation of toluene exhibited marked variation with the reaction times, even when these were quite short. The observed isomer distributions with reaction times of 10, 0.09, 0.03, 0.01 sec. were extrapolated to zero reaction time to obtain the isomer distribution in the absence of isomerization. From this isomer distribution, 41.1% *ortho*, 19.4% *meta* and 39.5% *para*, and the relative rate, $k_T/k_B$ 4.0, the partial rate factors for the benzylation reaction were calculated: $o_f$ 4.9; $m_f$ 2.3; $p_f$ 9.4. The data provide a fair fit with the Selectivity Relationship.

Methylation,[3] ethylation[3] and isopropylation[4] of toluene, under the catalytic influences of gal-

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(1) Directive Effects in Aromatic Substitution. XXXV.

(2) Post-doctorate research associate, 1956–1957, on a grant-in-aid provided by the American Cyanamid Co.

(3) C. R. Smoot and H. C. Brown, THIS JOURNAL, **78**, 6245, 6249 (1956); H. C. Brown and C. R. Smoot, *ibid.*, **78**, 6255 (1956).

(4) S. U. Choi and H. C. Brown, *ibid.*, **81**, 3315 (1959).