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# Catalytic Dehydrohalogenation on Alumina Modified with Alkali-Metal Chlorides

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The stopped-flow technique was used to elucidate the mechanistic scheme of dehydrobromination of 1-bromo-2-methylpropane on alumina modified with alkali-metal chlorides. The main product was 2-methylpropene, and it was found to be formed both directly from 1-bromo-2-methylpropane, and through isomerization of the latter to 2-bromo-2-methylpropane. Small amounts of water adsorbed on the surfaces increase the catalytic activity and decrease the retention volumes of the various substances. Hydrogen bromide produced in the reactions does not seem to affect the catalysts. Rate constants at various temperatures and Arrhenius parameters have been determined in order to compare the catalytic activity of the surfaces used.

## INTRODUCTION

In a previous paper (*1*) we employed the stopped-flow gas chromatographic technique of Phillips *et al.* (*2*) to study the dehydrohalogenation of three bromobutanes on a single catalytic surface, namely alumina modified with potassium bromide. In the present paper we have used the same technique for a kinetic investigation of four different surfaces using the dehydrohalogenation of only one bromobutane as a probe reaction. The surfaces studied consisted of activated alumina modified with four alkali-metal chlorides, i.e., salts differing only in their cation. The bromobutane chosen was 1-bromo-2-methylpropane, because it was found previously (*1*) to give almost exclusively one product, namely 2-methylpropene with no more than 1% of other isomeric butenes.

## EXPERIMENTAL

### *Materials*

Aluminum oxide active, acidic, Brockmann grade 1, for chromatographic analysis, BDH Chemicals Ltd. was used. This was sieved, the fraction 100–120 mesh being retained.

"Suprapur" sodium and potassium chlorides of E. Merck AG., anhydrous lithium chloride of Alfa Inorganics Inc., and cesium chloride at least 99.5% of Riedel-de Häen AG. were used without further treatment.

1-Bromo-2-methylpropane from two different sources ("purum" isobutylbromide of Fluka AG., and isobutylbromide "zur synthese" of E. Merck AG.) was used after gas chromatographic purification on a 10 ft × 3/8 in. preparative column filled with 20% carbowax 20 M on 60–80 mesh chromosorb P. This column was run into a Varian 1525c gas chromatograph equipped with an automatic fraction collector. Both products gave the same results. It should be noted in this connection that results obtained by the stopped-flow technique are very little influenced by the purity of the reacting substance (*3*).

In all experiments nitrogen (99.98% purity) was used as carrier gas. This was obtained from AGA CHROPEI and was dried by passing it through 4A molecular sieve.

### *Apparatus*

A Pye-Unicam Series 104 gas chromatograph, modified as shown in Fig. 1, was used in all experiments. The catalytic column was a common stainless-steel gas-chromatographic column of 5 mm i.d. and length varying from catalyst to catalyst (29–80 cm). Injectors G and G′ were heated at the same oven temperature as the columns.

The analytical column was either a 2.12 m × 2.5 mm (i.d.) column filled with dinonyl phthalate (15%) on chromosorb P 80–100 mesh, or a 2.15 m × 0.5 mm (i.d.) column filled with ethylene glycol-silver nitrate (saturated solution) 8% on chromosorb P 60–80 mesh.

In one position of the valves M and N the flow of the gases is that shown by the full lines in Fig. 1, and in the other position by the dotted lines.

The oven temperature was read on a calibrated mercury thermometer. Temperature variations in each experiment were less than ±0.1°C.

### *Procedure*

The kinetic runs were performed by the stopped-flow technique (*2*) after the conditioning of the columns. A small amount (0.5 μl) of the reacting substance was injected onto the catalytic column heated at constant temperature and connected to the flame ionization detector. Gas flow rates were 12 to 18 ml · $\text{min}^{-1}$, and the pressure drop about 130 mm Hg along a 80 cm column.

At precisely known times, measured from the moment of injection, the flow of the carrier gas through the column was stopped for known and always the same (usually 1 min) time intervals, by simultaneously closing valves D and D′. This procedure was usually started after the emergence of the head of the asymmetrical peak corresponding to the product of the reaction taking place on the catalytic surface. Following each restoring of the gas flow, one or more sharp symmetrical peaks (stop-peaks) were noted in the chromatographic trace (see Fig. 6).

The fraction of reactant molecules on the catalytic surface $f$ was determined by the relation $f = (g - 1)/g$, where $g$ is the ratio of the retention volume of the reactant to the dead volume of the column (*2*). The latter volume was determined by measuring the retention volume of methane which was negligibly adsorbed.

Identification of products and reactants was accomplished by means of the analytical column. At any desired position of the

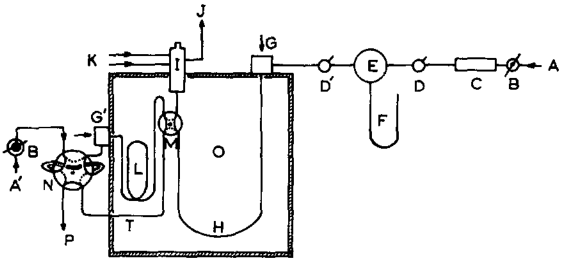


FIG. 1. Schematic arrangement for kinetic studies and identification of the substances emerging from the catalytic column. A,A′: carrier gas (nitrogen) for catalytic and analytical column, respectively, B: control valves, C: gas drying tube, D,D′: shut-off valves, E: volume reservoir, F: open manometer, G,G′: injector to catalytic and analytical column, respectively, O: gas-chromatograph oven, H: catalytic column, I: flame ionization detector, K: hydrogen and air to the detector, J: signal to amplifier and recorder, L: analytical column, M: four-port valve, N: six-port gas-sampling valve with a 5 ml loop, T: 2.5 mm (i.d.) tubing, P: to atmosphere.

reaction chromatogram both valves M and N (see Fig. 1) were switched to the "dotted" position. By then switching valve N to the other position, the contents of the loop were swept into the analytical column and thence to the detector. Reference samples for identification were introduced through injector G′.

### *Preparation of the Catalysts and Conditioning of the Columns*

The method of preparation of the catalysts and the conditioning of the columns described in another paper (*1*) were slightly modified for the reasons discussed in the Results section.

Aluminum oxide (100–200 mesh, 45 g) was added to the modifier salt solution (35 ml containing 5 g of alkali chloride). The resulting mixture was left for 24 hr at room temperature in a beaker. After this period the water was removed on a steam bath, and the solid remained was spread on a filter paper and left for another 24 hr period. This was followed by sieving, the 100–120 mesh fraction being retained.

The conditioning of each catalyst was carried out *in situ* by heating the catalytic column in a stream of carrier gas (15 ml · min$^{-1}$) for two successive 30-min periods at 100 and 200°C.

## RESULTS AND DISCUSSION

### *The Effects of Water and Hydrogen Bromide on the Chromatographic and Catalytic Properties*

It was observed earlier (*1*) that an "aging" period of about 8 hr was required in order to achieve constant characteristics of the catalyst. In the present paper we also found that, if this period were omitted, chromatograms like that of Fig. 2(a) were obtained at 60–150°C. These showed some new peaks other than those corresponding to the main product and the reactant. Moreover the form of the chromatograms was continually changing with time and with the number of preceding injections. Finally the form shown in Fig. 2(b) was obtained and this remained unchanged. The above facts can be explained by assuming that the high temperature heating activated thermodynamically irre-

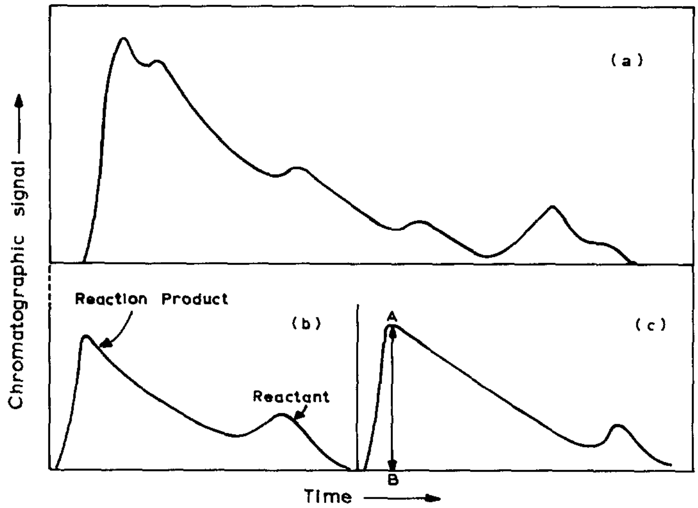


FIG. 2. Simple elution chromatograms of 1-bromo-2-methylpropane on catalytic columns prepared and conditioned by three different ways: (a) catalyst prepared as reported earlier (*1*) immediately after heating at temperatures above 250°C for 10 hr; (b) the same catalyst after staying for a few days at lower temperatures (60–150°C); (c) catalyst prepared as described in the experimental section immediately after heating at 200°C for 1 hr in a stream of carrier gas (15 ml · min$^{-1}$).

versible defects of high activation energy. These could be responsible for side reactions thus giving the complicated picture of Fig. 2(a). Aging of the catalyst at a lower temperature probably leads to the disappearance of these defects with the result of Fig. 2(b).

By preparing the catalyst as described in the experimental section and heating it only for 1 hr at 200°C the picture of Fig. 2(c) was obtained. This is similar in form with Fig. 2(b). However, the retention volume of the product and reactant decreased with time, whilst catalytic activity, as approximately measured by the height of the product peak [distance *AB* in Fig. 2(c)] increased with time. These facts were attributed to traces of water adsorbed on the catalytic surface during the period following thermal activation. This was confirmed by injecting small amounts of water onto the column followed (after about 10 min) by injection of 1-bromo-2-methylpropane. The results are shown in Fig. 3, and indicate that water acts indeed in opposite directions on retention volume and on activity. The effect of water on the catalytic activity was also proved by determining the rate constant of the reaction, at the same temperature, as a function of the amount of water added.

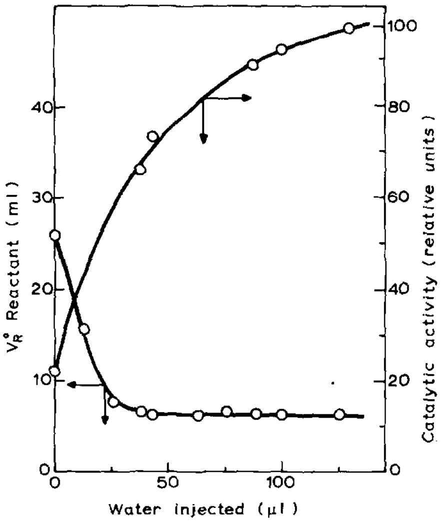


FIG. 3. Effect of injected water on the retention volume and the catalytic activity of 10% $KCl/Al_2O_3$ for the dehydrohalogenation of 1-bromo-2-methylpropane at 112°C. The catalyst was prepared as described in the experimental section and then activated at 200°C for 1 hr.

From Fig. 3 one is inclined to believe that addition of water to the activated catalyst is an attractive method to bring it to regions of constant chromatographic and catalytic behavior. This, however, is not the case, because the water added is weakly held on the surface and desorbs easily, bringing the catalyst back to regions of instability. The desired stability was simply achieved by less activation (30 min at 100°C and 30 min at 200°C as mentioned).

The changing form of the chromatograms with increasing number of preceding injections of the reacting substance points to the possibility that hydrogen bromide produced in the reaction influences the catalytic surface. However, injections of hydrogen bromide before injection of the reactant showed that both the retention volume of the reactant and the catalytic activity remained practically unaffected. Only the retention volume of the product shows a small increase with increasing amounts of injected hydrogen bromide. This increase, however, should be very small when microgram quantities of reactant are used.

### *Phenomena Observed with Potassium Chloride as a Modifier*

A 29 cm column was originally used with alumina modified by 10% w/w potassium chloride. In the temperature region 50–110°C most chromatograms obtained by the simple elution technique had the form of Fig. 2(b), i.e., showed one product and one reactant peak only, while in those obtained by the stopped-flow technique an extra sharp peak appeared after each stopping and restoring of the carrier gas. However, between 70 and 80°C and after a certain time from the start of the reaction, two stop-peaks followed one and the same stop of the carrier gas. That could be due to local inhomogeneities of the surface along the column, but this was excluded by reversing the catalytic column when exactly the same picture as before was observed. The possibility of parallel reactions giving two products with a common reactant is also excluded by the fact that the difference in the retention times of the two stop-peaks increased with time, contrary to what one would expect in a situation of parallel reactions, since the common reactant, approaching the end of the column with time, would leave smaller and smaller column length for the separation of the two products.

A plot of the logarithm of the area $S$ of the stop-peaks against time $t$ according to the equation

$$\log S = \text{constant} - \frac{kf}{2.303}\,t \qquad (1)$$

($f$ being the fraction of reactant molecules on the catalytic surface) should give a straight line for simple first-order reactions (*1*,*2*). The same linear relationship is expected for parallel first-order reactions by plotting either one or the two combined stop-peaks. Figure 4 shows this plot for 100.0°C. Separation of the two peaks does not occur at this temperature. The leveling of the plot at times longer than about 15 min shows a rather more complicated reaction scheme than two simple parallel first-order processes.

By increasing the length of the column to 80 cm, in order to achieve better separation between the two stop-peaks, and then plotting log $S$ against time separately for each peak, straight lines like those of Fig. 5 were obtained. These lines explain the form of plots of Fig. 4, and indicate the existence of two separate reactions, one being first-order and the other zero-order or first-order with a very small rate constant.

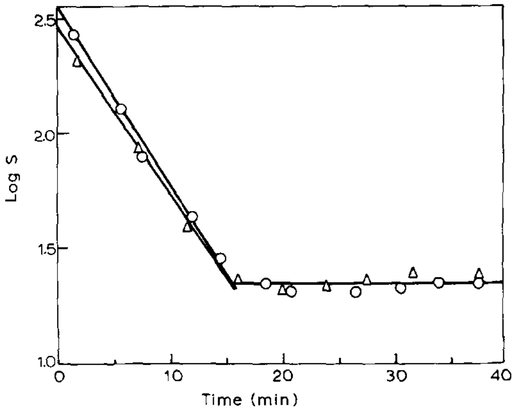


FIG. 4. The plot of Eq. (1) for the dehydrobromination reaction of 1-bromo-2-methylpropane on 10% $KCl/Al_2O_3$ at 100.0°C. ○ and △ represent points from two identical runs.

Parallel first-order reactions with a common reactant being excluded for the reasons previously stated, there remain three major possibilities: (a) isomerization of the first product (which was identified as 2-methylpropene) to give another product, (b) depolymerization of an initially formed polymer to give the same monomeric product, and (c) a side reaction of the initial reactant to give another reactant from which the same or another butene is obtained by an elimination reaction.

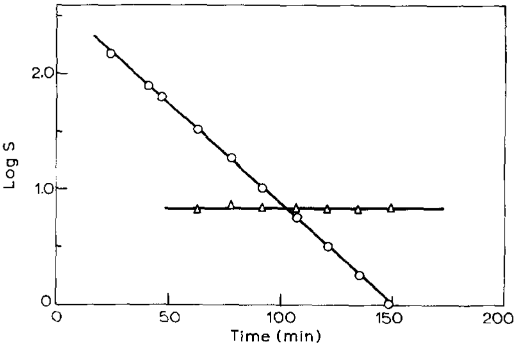


FIG. 5. The plot of Eq. (1) for the dehydrobromination reaction of 1-bromo-2-methylpropane on 10% $KCl/Al_2O_3$ at 79.0°C performed with a 80 cm column, ○ stop-peaks appearing from the beginning of the reaction; △ second stop-peaks appearing after a certain time from the start of the reaction.

Possibilities (a) and (b) were excluded by injecting pure 2-methylpropene onto the column, when no stop-peak appeared, and also by using stops of different duration, when no change in the first-order plots was observed.

A side reaction of the injected bromobutane giving a different reactant can conceivably be an isomerization to another bromobutane, a hydrolysis to a butanol, or an exchange of the bromine with a chloride ion of the catalyst to give a chlorobutane. All these reaction schemes can lead to simple first-order kinetics provided that the first step is fast and not rate-controlling. In further support of possibility (c) above, it was observed that at the lowest working temperature two chromatographic bands of reactants were eluted from the column.

More information about the mechanistic scheme of the reaction was obtained with the next catalyst, in favor of a fast isomerization of 1-bromo-2-methylpropane to another bromobutane which on dehydrobromination gives the same butene as the original reactant.

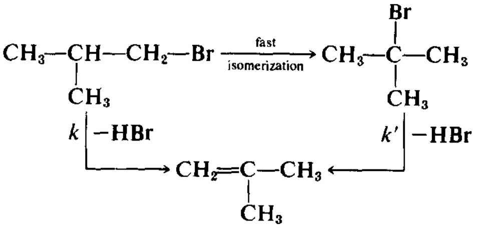
## *Phenomena Observed with Lithium Chloride as a Modifier*

A 80 cm column, filled with alumina modified by 10% lithium chloride, was used. The stopped-flow technique gave chromatograms like that shown in Fig. 6. The two stop-peaks were better separated than in the previous catalyst and the two bands, corresponding to two different reactants, appeared in the temperature range 85–95°C.

It is noteworthy that, after the elution of the first reactant band, only one stop-peak was observed, whilst after the emergence of the second reactant band no stop-peak was noted. The plot of log $S$ against time for each product separately, according to Eq. (1), showed two first-order reactions with different rate constants.

It was found by analysis (as described in the last paragraph of the procedure in the experimental section) that the two products were identical, namely 2-methylpropene, and that the second reactant band corresponds to the injected 1-bromo-2-methylpropane, whilst the first reactant band is 2-bromo-2-methylpropane.

All these findings are consistent with the following reaction scheme:



$$\begin{array}{ccc} CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2-Br & \xrightarrow[\text{isomerization}]{\text{fast}} & CH_3-\overset{\displaystyle Br}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}-CH_3 \\ k \downarrow -HBr & & k' \downarrow -HBr \\ & CH_2=\underset{\displaystyle CH_3}{\underset{|}{C}}-CH_3 & \end{array} \qquad (2)$$

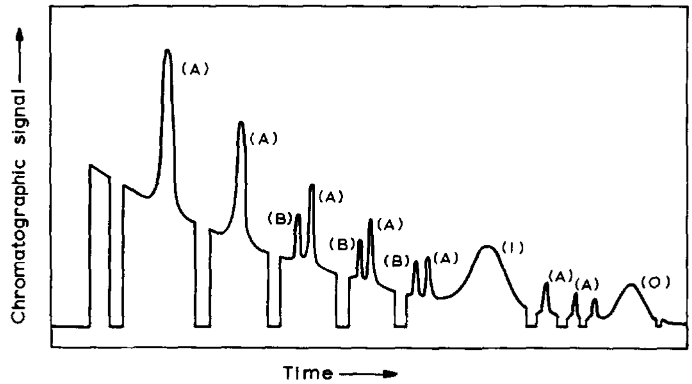


FIG. 6. A schematic representation of a typical chromatogram for the dehydrobromination of 1-bromo-2-methylpropane on 10% LiCl/$Al_2O_3$. A: First stop-peak produced from O; O: Original reactant; B: Second stop-peak produced from I; I: Isomerized reactant.

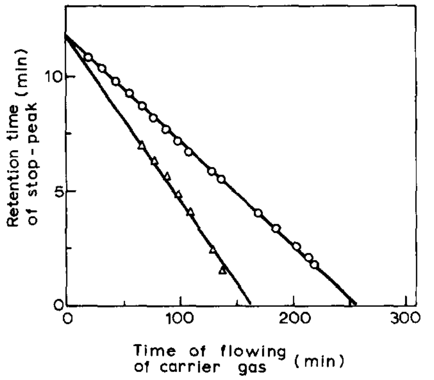


FIG. 7. The retention time of each stop-peak plotted as a function of time of flowing of the carrier gas through the column. The latter time is found by measuring the time elapsing between injection of the reactant and stopping of the carrier gas flow, and then subtracting the time during which the carrier gas was not flowing. △ and ○ refer to the two product peaks, appearing first and second, respectively, after restoring the carrier gas flow. The reaction was carried out at 80.0°C on 10% $LiCl/Al_2O_3$.

The last question to be answered is which of the two experimentally found rate constants is $k$ and which is $k'$. This was most conveniently found by plotting the retention time of each stop-peak (measured from the moment of restoring the carrier gas flow) against the time of flowing of the carrier gas through the column (measured from the moment of injection of the reactant to the moment of the corresponding stop). Such a plot is shown in Fig. 7, and it is very informative, particularly as regards the extrapolation of the two straight lines to both axes. The intercept on the ordinate (corresponding to zero volume of carrier gas having flowed through the column) is the same for both products, as expected in view of the fact that the two products are chemically identical and their parent compounds have not yet been separated by the column. The other intercepts on the abscissa (corresponding to zero retention volume of each product) predict the retention times of the corresponding parent compounds. For the run of Fig. 7 these are estimated to be 164 and 258 min, whereas the experimental values are 160 and 256 min, respectively. The conclusion follows, without much doubt, that the product peaks appearing first after each restoring of the gas flow originate from the reactant first eluted from the column (2-bromo-2-methylpropane), whilst the product peaks appearing last come from the second reactant (1-bromo-2-methylpropane). Therefore, rate constants determined from plots of the first peak correspond to $k'$, and those determined from plots of the second peak refer to $k$.

Figure 7 also explains why the products appear to be two only after a certain time, showing that this is due to insufficient initial separation of the two peaks, because their retention times are identical at first, their difference increasing with time.

The linearity of the plots of Fig. 7 deserves some comment. The slope of each plot is equal to $-t_R^p/t_R^r$ where $t_R^p$ and $t_R^r$ are the intercepts on the ordinate and the abscissa, respectively. Taking into account that these represent the corrected retention times of the product and the reactant, respectively, corresponding to the total weight of the adsorbent, $W$, and making use of the relations $V_R = \dot{V} t_R$ and $V_R = W\beta$, where $V_R$ is the corrected retention volume, $\dot{V}$ the volume flow rate and $\beta$ the partition coefficient of the vapour, we obtain for the slope of the plots:

$$\text{slope} = -\frac{t_R^p}{t_R^r} = -\frac{V_R^p}{V_R^r} = -\frac{\beta^p}{\beta^r}. \qquad (3)$$

Thus, the constant slope of the plots means that the ratio of the partition coefficient of the product, $\beta^p$, to that of the corresponding reactant, $\beta^r$, remain constant throughout the entire length of the column, this being an indication of the uniformity of the surface.

### *Phenomena Observed with Sodium Chloride and Cesium Chloride as Modifiers*

A 55 and a 50 cm column was used with sodium chloride and cesium chloride modifiers, respectively. The same phenomena as with the previous catalyst were observed, thus showing that the same mechanism is operative on all surfaces studied. Moreover, it was found that the fraction of the reactant isomerizing to 2-bromo-2-methylpropane varies from 0 to 100% depending on the surface studied, and temperature, increasing with the latter.

A detailed study of the effect of varying percentages of modifiers has not been made, but it was checked in our previous communication (*1*) that a 9–10% (w/w) modification brings the surface to a region of constant activity with respect to modifier proportion. The 10% modification used throughout the present work corresponds to a millimole per gram proportion ranging from 0.66 (CsCl) to 2.6 (LiCl). On comparing these values with those reported by Maatman and Griend (*4*), we see that our modification proportion is far above the range within which activity vanishes for the decomposition of 1-butanol. Therefore, our surfaces are not comparable with those prepared by the above authors, this probably being due to the different method of impregnation and/or activation.

TABLE 1

RATE CONSTANTS FOR DEHYDROBROMINATION OF 1-BROMO-2-METHYLPROPANE ($k$) AND OF 2-BROMO-2-METHYLPROPANE ($k'$) ON 10% $LiCl/Al_2O_3$

| Temperature (°C) | $k \cdot 10^2$ (min$^{-1}$) | $k' \cdot 10^2$ (min$^{-1}$) |
|---|---|---|
| 80.0 | 1.77 ± 0.01 | — |
| 85.9 | 4.4 ± 0.1 | — |
| 92.4 | 7.6 ± 0.1 | — |
| 102.4 | — | 0.77 ± 0.03 |
| 105.0 | — | 0.82 ± 0.04 |
| 116.9 | — | 2.89 ± 0.07 |
| 121.5 | — | 5.8 ± 0.1 |

## *Rate Constants and Arrhenius Parameters for the Reactions*

Tables 1 and 2 compile rate constants on all four surfaces at various temperatures, as determined from the slopes of plots of Eq. (1) and the corresponding values of $f$. The latter were ranging from 0.9884 to 0.9984. Rate constants denoted by $k$ correspond to the direct dehydrobromination of 1-bromo-2-methylpropane, whilst $k'$ refers to dehydrobromination of 2-bromo-2-methylpropane, as indicated in the reaction scheme (2). All errors in these and the following Tables are standard errors.

Rate constants, determined by the stopped-flow technique are directly comparable, because they are true rate constants of the surface reaction, and are in-

TABLE 2

RATE CONSTANTS FOR DEHYDROBROMINATION OF 1-BROMO-2-METHYLPROPANE ON $Al_2O_3$ MODIFIED BY VARIOUS SALTS (10%)

| $NaCl/Al_2O_3$ | | $KCl/Al_2O_3$ | | $CsCl/Al_2O_3$ | |
|---|---|---|---|---|---|
| Temperature (°C) | $k \cdot 10^2$ (min$^{-1}$) | Temperature (°C) | $k \cdot 10^2$ (min$^{-1}$) | Temperature (°C) | $k \cdot 10^2$ (min$^{-1}$) |
| 91.7 | 0.21 ± 0.03 | 65 | 1.13 ± 0.04 | 63.5 | 1.33 ± 0.08 |
| 100.4 | 0.38 ± 0.04 | 69.1 | 1.51 ± 0.05 | 71.2 | 2.18 ± 0.03 |
| 104.6 | 0.69 ± 0.05 | 73.1 | 2.13 ± 0.06 | 85.3 | 9.1 ± 0.2 |
| 112.4 | 1.7 ± 0.7 | 82.4 | 4.3 ± 0.1 | 89.3 | 12.1 ± 0.3 |
| 118.3 | 2.7 ± 0.1 | 82.4 | 4.5 ± 0.1 | 102.9 | 20 ± 5 |
| 123.4 | 4.5 ± 0.1 | 88.6 | 6.9 ± 0.3 | | |
| | | 91.7 | 12 ± 1 | | |
| | | 91.7 | 11.3 ± 0.3 | | |
| | | 100.0 | 17.6 ± 0.1 | | |
| | | 100.0 | 16 ± 1 | | |

TABLE 3

ACTIVATION ENERGIES (*E*) AND FREQUENCY FACTORS (*A*) FOR DEHYDROBROMINATION OF 1-BROMO-2-METHYLPROPANE ON $Al_2O_3$ MODIFIED BY VARIOUS SALTS (10%)

| Catalyst | Surface area ($m^2g^{-1}$) | $E$(kcal · mole$^{-1}$) | log $A$ ($A$ in min$^{-1}$) |
|---|---|---|---|
| $LiCl/Al_2O_3$ | 81.5 | 30.2 ± 0.5 | 16.9 ± 0.3 |
| $NaCl/Al_2O_3$ | 105.5 | 29 ± 1 | 14.5 ± 0.7 |
| $KCl/Al_2O_3$ | 104.6 | 20.1 ± 0.7 | 11.1 ± 0.5 |
| $CsCl/Al_2O_3$ | 85.2 | 19 ± 2 | 10 ± 1 |
| $LiCl/Al_2O_3$[a] | 81.5 | 31 ± 3 | 16 ± 2 |

[a] The values in this line refer to dehydrobromination of 2-bromo-2-methylpropane.

dependent of the surface area of the solid. Anyhow, the surface area of the catalysts, determined as described elsewhere (*1*), are given in Table 3, together with the Arrhenius parameters for the reactions as determined from Arrhenius plots

Surface areas differ little from catalyst to catalyst, and there seems to be no regular dependence of the surface area on the nature of the modifier cation.

As regards Arrhenius parameters, it is evident that in going from cesium to lithium chloride as a modifier there is a considerable increase in the energy of activation for the dehydrohalogenation of 1-bromo-2-methylpropane, but this is compensated by a corresponding increase in the frequency factor, so that rate constants at the same temperature do not differ greatly from one another.

A correlation of the Arrhenius parameters with the heat of adsorption was made in our previous communication (*1*), for different reacting substances on the *same* catalyst ($KBr/Al_2O_3$). A similar correlation does not seem to hold in the present paper, conceivably because we have studied the reaction of the same substance on *different* catalysts.

## ACKNOWLEDGMENT

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