

Catalytic Dehydrohalogenation of Bromobutanes Studied by Stopped-Flow Gas Chromatography

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Dehydrohalogenation reactions of bromobutanes on alumina modified with potassium bromide were studied by the stopped-flow technique. Isomerization and polymerization reactions of the products were kept to a minimum. The reactions were first-order with respect to the reactant. From 1-bromobutane all four possible alkenes were produced, 1-butene being the main product. From 1-bromo-2-methylpropane almost exclusively 2-methylpropene was obtained, whereas 2-bromobutane gave *cis*- and *trans*-2-butene in about equal amounts. The heat of adsorption of the first two bromides was determined and this was correlated with the Arrhenius parameters to interpret the compensation effect observed. From this correlation certain conclusions about the mechanism of the reactions are drawn. The results are consistent with a two-step mechanism, the second step being rate determining.

Detailed studies of dehydrohalogenation reactions over solid catalysts are not abundant in the literature. Little is known about the mechanisms of these reactions. They are reviewed in a recent article by Noller, Andréu and Hunger (1), who list most of the relevant literature. In addition, one may mention some more work by Mochida, Kato and Seiyama (2), and by Lopez and co-workers (3) and Rosa-Brusin *et al.* (4). Most of these studies were performed by the so-called microcatalytic technique (5), which utilizes gas chromatography for the analysis of the products. The possibility of studying adsorption during surface catalysis with the gas chromatographic technique has been pointed out by Tamaru (6). Bassett and Habgood (7) placed this on a quantitative basis and showed how the chromatographic method permits a determination of the extent of adsorption of the reactant under reaction conditions, and thus of the rate constant for the reaction on the catalytic surface. Their mathematical treatment applies only to first-order reactions. Phillips *et al.* (8) have further

explored the possibilities of using an adsorbent surface simultaneously as a catalyst and as a chromatographic column, and developed a method for direct study of heterogeneous catalysis by gas-solid chromatography. This latter method is very attractive, since it leads to very accurate rate constants for the surface reaction from which true activation energies can be calculated. We have successfully used the method of Phillips *et al.* (8) to study dehydrobromination reactions of 1-bromobutane, 2-bromobutane and 1-bromo-2-methylpropane over alumina modified with potassium bromide (9.1% KBr). These modified surfaces, developed by Scott and Phillips (9), are very suitable for gas-solid chromatography and lend themselves to the application of the method.

EXPERIMENTAL METHODS

Preparation of Catalysts

Materials. Aluminum oxide for chromatography (Fluka AG., type 504C, acidic) was used. This had the following charac-

teristics: pH in water suspension, 4.5 ± 0.3 ; activity stage 1 (according to Brockmann); surface area, $155 \text{ m}^2 \text{ g}^{-1}$ (BET, N_2 at 77°K); statistical mean particle diameter 0.13 mm.

Potassium bromide (E. Merck, "suprapur") was employed as such.

Tri-distilled water was used in all catalyst preparations.

Procedure. The aluminum oxide was sieved, the fraction 100–120 mesh being retained. To this (12 g) an aqueous solution of potassium bromide (4 ml, 30% w/v) was added dropwise, and the mixture, after shaking, was left for 16 hr at room temperature. After this period it was dried, being kept in a furnace for three successive 1-hr periods at 100, 200 and 255°C . It was sieved again and the fraction 100–120 mesh (ca. 10 g) was retained. The above procedure was repeated 16 times; the resulting solids were well mixed and used in most experiments. This catalyst is referred to as No. 22. Another catalyst prepared in a smaller amount by the same method is labeled No. 21.

Kinetic Runs

Materials. Fluka AG. 1-bromobutane ("puriss"), 2-bromobutane ("purum"), and 1-bromo-2-methylpropane ("purum") were purified by preparative gas chromatography using a 10 ft \times $\frac{3}{8}$ in. column filled with 20% carbowax 20M on 60–80 mesh chromosorb P. This was fitted into a Varian 1525c gas chromatograph equipped with an automatic fraction collector.

Helium (Union Carbide 99.99%) was dried by passing it through a molecular sieve tube.

Instrument. The above-mentioned gas chromatograph, equipped with flame ionization and thermal conductivity detectors, was slightly modified so as to include a gas shutoff valve before the injector for closing and opening the carrier gas, and a mercury manometer for measuring the pressure drop along the column. A 1-liter reservoir was also included between the gas cylinder and the chromatograph to prevent inlet pressures from rising appreciably during the stopped-flow periods, which in-

variably were 1 min. This was also assisted by closing a second gas shutoff valve placed immediately after the gas pressure regulator. Under these conditions pressure variations during closing and opening the gas flow were less than 1 mm Hg.

The oven temperature was monitored by three thermocouples in series, placed at different points along the chromatographic column, and connected to a suitable potentiometer. Temperature variations were less than 0.2°C . Several measurements were taken during each kinetic run; their mean value was recorded.

Columns and conditioning. Two stainless-steel columns were used, differing only in dimensions. The first was a 30 cm \times 6.4 mm (o.d.) column and was employed in the runs with 1-bromobutane and 1-bromo-2-methylpropane. The second column, 1 m \times 3.2 mm (o.d.), was used with 2-bromobutane in order to achieve better separation of the *cis*- and *trans*-2-butene produced by dehydrohalogenation. This column, used with the first two bromides, showed one product peak only and the reactants did not appear in the chromatograms, obviously owing to high conversion to products. Therefore, it was found more convenient to use the first shorter column for these bromides. The amount of catalyst used was ca. 5.5 and 6.5 g in the first and second columns, respectively.

The conditioning of the catalyst was performed *in situ* at 255°C for 6 to 10 hr with carrier gas (He) passing through the column at a superficial or filter-flow velocity (i.e., not correcting for the fraction of void space around the particles) of 109 cm min^{-1} . This was followed by heating for at least 8 hr (usually 10) at 100°C . Longer heating was found unnecessary, since after 3 hr at 255°C and 8 hr at 100°C the characteristics and behavior of the catalyst remain constant. For the final catalytic activity it was immaterial whether trial injections of reactants were made during the heating period or not.

Whenever a new catalytic column was prepared and conditioned a different capital letter was added to the number of the catalyst, with which the column was filled,

e.g., catalyst No. 22B denotes the second column prepared with catalyst No. 22.

Procedure. The catalytic runs were performed immediately after the conditioning of the columns by injecting 0.5 to 1 μ l of liquid through a heated injector (100–110°C). It was found that three such injections suffice to establish constant catalytic activity at each temperature. The superficial velocity of the carrier gas, measured at column outlet pressure, was 109 cm sec⁻¹ as mentioned before. This required a pressure drop along the column of 8–9 cm and 61 cm Hg for the 30 cm \times 6.4 mm and 1 m \times 3.2 mm column, respectively. Detection of products and reactants was accomplished by one of the flame ionization detectors of the instrument. The fraction of reactant molecules on the catalytic surface f was determined in separate runs under the same conditions using a thermal conductivity detector in order to determine the dead volume of the column. If g is the ratio of the retention volume of the reactant to the dead volume of the column, then $f = (g - 1)/g$ (8).

Identification of Products

The identification of isomeric butenes produced by the reactions of the three bromobutanes studied has been accomplished by an additional analytical column 95 cm \times 3.2 mm (o.d.) filled with ethylene glycol–silver nitrate (3.77:1; w/w) 24% on chromosorb P 60/80 mesh. This was connected in series to the 30 cm \times 6.4 mm catalytic column and the combined columns were operated under conditions similar to those used in the actual catalytic runs. A working temperature of 100°C was selected for 1-bromobutane and 1-bromo-2-methylpropane, while for 2-bromobutane this was 80°C. Pure gaseous butenes (Fluka AG. "purum") were used as standards.

Surface Area and Pore Volume Measurements

A Perkin-Elmer Sorptometer Model 212-D was employed in surface area and pore volume measurements. Pure nitrogen (Union Carbide 99.99%) was used as ad-

sorption gas, and helium (Union Carbide 99.99%) as carrier gas.

After the last kinetic run, each catalyst was heated for 16 hr at 250°C with carrier gas running through the column, and ca. 0.1 g of the dry material was used for measurements. In each surface area determination a BET plot of three to four points (relative nitrogen pressures 0.1 to 0.3) was constructed. The results are given in Table 4.

RESULTS

The simple elution technique and the stopped-flow technique in the method of Phillips *et al.* (8) both applied to 1-bromobutane gave the same results. The second technique was employed throughout the present work. However, a constant stopped-flow interval (1 min) of the carrier gas was used in each run, with two advantages. First, no correction was necessary to reduce the observed stopped-flow time to the real stopped-flow time, the difference between the two being due to no instantaneous stopping and reestablishment of the normal flow conditions. Second, provided the reaction is first-order, the rate equation assumes a linear form. This is so because, according to the above-mentioned paper (8), for a first-order reaction the amount of product formed in a stopped-flow interval is given by the relation:

$$(\text{Product}) = bS = ae^{-kfvt} \sinh(kfv) \quad (1)$$

In this equation, b is a proportionality constant, S represents the area of the peak resulting from the stopped-flow interval, a is the amount of reactant injected, k the reaction rate constant, f the fraction of reactant molecules on the surface, v is half of the stopped-flow interval and t the midtime of the interval.

By taking logarithms and keeping v constant throughout a run, Eq. (1) reduces to the simple linear form:

$$\log S = \text{constant} - \frac{kf}{2.303} t. \quad (2)$$

In all kinetic runs the plots of $\log S$ versus t were linear at each temperature, as required by Eq. (2), showing that the reac-

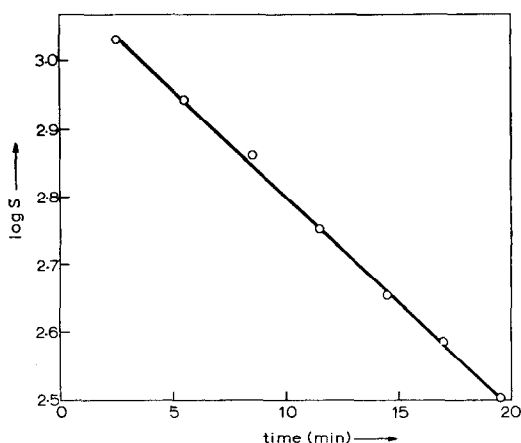


Fig. 1. Kinetic run for dehydrohalogenation of 1-bromobutane on 9.1% $\text{KBr}/\text{Al}_2\text{O}_3$ (catalyst No. 22A) at 114.3°C .

tions were simple first-order. An example is given in Fig. 1. Having determined f in separate experiments (see Experimental Methods section), we calculated k from the slope of the above plots.

By using different stopped-flow intervals in the same run and the equation $\ln(S_1v_2/S_2v_1) = kf(t_2 - t_1)$, as described (8), rate constants identical with those obtained by means of Eq. (2) were calculated.

It is well known that many adsorbent columns, particularly at high temperatures, cause isomerization of alkenes. This effect must have been negligible in the present case, since we found that variation of the linear velocity of carrier gas within wide ranges (from 40 to 240 cm min^{-1}) had no effect on our results. This was also shown by comparison of the results obtained with the straight elution and the stopped-flow techniques, as previously mentioned. Furthermore, it was confirmed by injections of pure alkenes onto the column.

In order to keep polymerization of the alkenes to a minimum, advantage was taken of the fact that this reaction is a bimolecular one and therefore becomes negligible if the concentration of the alkenes produced is low. This was achieved by using short stopped-flow intervals (1 min).

In the case of 1-bromobutane and

1-bromo-2-methylpropane, where the remaining reactants were eventually eluted from the column, the elution peaks were fairly symmetrical showing that we were working in the linear part of the isotherm. This was not unexpected, since the vapor pressures of the reactants above the catalyst surface were very low, resulting in low surface coverage.

Finally, we have found that the results were not altered by using glass, aluminum or stainless-steel columns.

Reproducibility of rate constants with catalytic columns prepared from the same catalyst batch was of the order of $\pm 5\%$, while with columns prepared from different batches the reproducibility can be inferred from Table 1, where results from two catalyst preparations (21 and 22) are given.

Kinetic runs with 1-bromobutane. All four butenes are produced in the proportion 83.7% 1-butene + *cis*-2-butene, 13.4% *trans*-2-butene and 3.0% 2-methylpropene. The separate determination of the first two could not be achieved with adequate accuracy.

Using only the catalytic column the four butenes appeared as a single symmetrical peak, so that an overall rate constant k was determined from the stopped-flow experiments.

Table 1 lists the results obtained with two catalysts. The temperature was varied in a random manner, the runs being conducted after 0.5-hr stabilization at each temperature and after a few trial injections to establish constant catalytic activity. The values of f given in Table 1 were calculated from the plot of the experimental values of f versus temperature (Fig. 2). These plots were to a good approximation linear.

In spite of the fact that k here is an overall rate constant, the plots of $\log k$ versus $1/T$ (Fig. 3) were approximately linear, showing that the Arrhenius parameters are not very different for the formation of different products from the same reactant. These parameters are listed in Table 4. In Table 4 we also give the surface area and pore volume of each catalyst, as well as the heat of adsorption of the reac-

TABLE 1
RATE CONSTANTS FOR DEHYDROHALOGENATION OF 1-BROMOBUTANE ON 9.1% KBr/Al₂O₃ CATALYSTS,
AT VARIOUS TEMPERATURES^a

Catalyst No. 21A			Catalyst No. 22A		
Temp (°C)	<i>f</i>	<i>k</i> × 10 ² (min ⁻¹)	Temp (°C)	<i>f</i>	<i>k</i> × 10 ² (min ⁻¹)
99.6	0.9805	2.51 ± 0.03	99.3	0.9792	1.5 ₀ ± 0.09
99.6	0.9805	2.34 ± 0.04	105.1	0.9737	2.94 ± 0.07
106.7	0.9753	4.7 ± 0.1	109.8	0.9693	4.2 ± 0.1
112.5	0.9710	6.5 ± 0.2	114.3	0.9650	7.46 ± 0.06
119.3	0.9661	11.4 ₀ ± 0.09	119.0	0.9606	11.7 ± 0.2
123.5	0.9631	14.5 ± 0.7	128.9	0.9512	17.7 ± 0.4
124.7	0.9622	15.6 ± 0.3	134.6	0.9458	26.8 ± 0.6
124.7	0.9622	16.0 ± 0.2	139.7	0.9410	37 ± 1
129.2	0.9590	16.5 ± 0.3	143.9	0.9370	53 ± 2
132.0	0.9569	21.0 ± 0.5			
135.5	0.9543	25.9 ± 0.6			

^a All errors given in this and the following Tables are "probable errors," i.e., confidence limits at the 50% level of significance.

tants. This was calculated from the variation of the retention volume with temperature, determined in the same runs used to evaluate *f*. All necessary corrections for compressibility of the carrier gas, column temperature, etc., were applied in the calculation of retention volumes.

Kinetic runs with 1-bromo-2-methylpropane. This reactant gave almost exclusively 2-methylpropene with a negligible amount (less than 1%) of *trans*-2-butene. Table 2 compiles the results obtained after 1-hr

stabilization at each temperature. The *f* values were calculated as previously stated (Fig. 2). The relevant Arrhenius plot is shown in Fig. 4 and the calculated activation energy and frequency factor are given in Table 4.

Kinetic runs with 2-bromobutane. Two products were detected: one was identified as *trans*-2-butene, and the second as *cis*-2-butene containing probably some amount of 1-butene. Using only the catalytic column the two products appeared as

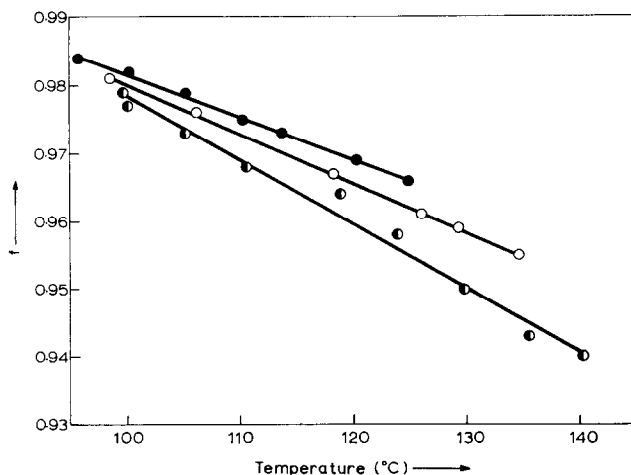


FIG. 2. Variation of *f* with temperature. (○) 1-Bromobutane/catalyst 21A; (◐) 1-bromobutane/catalyst 22A; (●) 1-bromo-2-methylpropane/catalyst 22E.

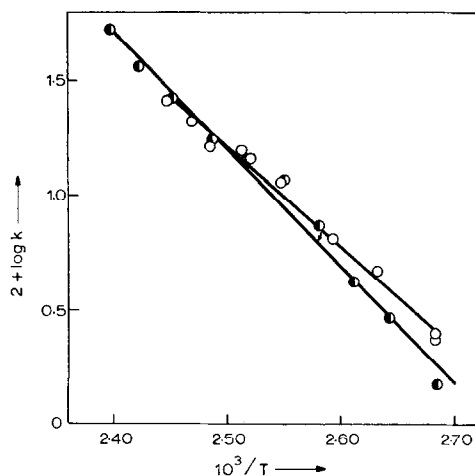


FIG. 3. Arrhenius plots for dehydrohalogenation of 1-bromobutane on 9.1% KBr/Al₂O₃. (○) Catalyst No. 21A; (●) catalyst No. 22A.

two separate symmetrical peaks after each stopped-flow interval. The remaining reactant was eluted from the column only after a long time, and therefore its f value was taken as approximately equal to unity. Before each new temperature setting the catalytic column was purged with carrier gas at 150°C for 1 hr to clean it from the

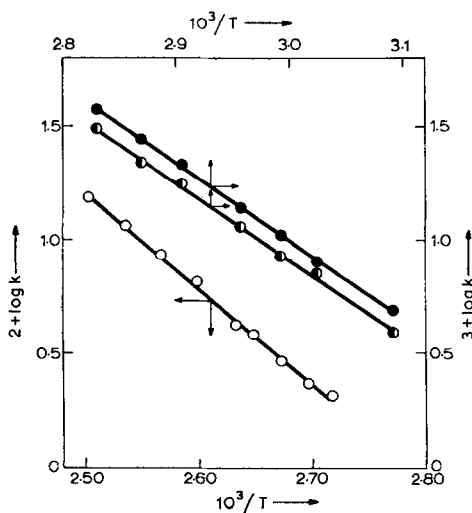


FIG. 4. Arrhenius plots for dehydrohalogenation on 9.1% KBr/Al₂O₃ of 1-bromo-2-methylpropane (○) (Catalyst No. 22E); and of 2-bromobutane (catalyst No. 22B), giving *cis*-2-butene (●), and *trans*-2-butene (●).

TABLE 2
RATE CONSTANTS FOR DEHYDROHALOGENATION OF 1-BROMO-2-METHYLPROPANE ON 9.1% KBr/Al₂O₃, AT VARIOUS TEMPERATURES (CATALYST No. 22E)

Temp (°C)	f	$k \times 10^2$ (min ⁻¹)
94.9	0.9850	2.06 ± 0.07
97.8	0.9832	2.31 ± 0.08
101.2	0.9810	2.92 ± 0.03
104.5	0.9789	3.8 ± 0.1
106.9	0.9774	4.3 ± 0.1
111.8	0.9743	6.59 ± 0.04
116.6	0.9713	8.6 ± 0.1
121.3	0.9683	11.59 ± 0.08
126.6	0.9649	15.4 ± 0.1

unreacted 2-bromobutane of the previous run. This was followed by 1-hr stabilization at each working temperature.

Overall rate constants $k = k_{trans} + k_{cis}$ were determined separately from both products; the ratio of their peak areas remained fairly constant at each temperature. These rate constants are listed in Table 3 and it is seen that the difference between values calculated from the two products are not statistically significant. From the mean values of the ratio of the two peak areas, the ratio k_{cis}/k_{trans} was calculated and was found to be in the range 1.20 to 1.27 with one exception at 57.5°C (1.14). From these ratios and the respective mean values of the two overall rate constants at each temperature, k_{trans} and k_{cis} were computed and are given in Table 3. Finally the Arrhenius plots for production of *cis*- and *trans*-2-butene are drawn in Fig. 4 and the relevant Arrhenius parameters are again included in Table 4.

DISCUSSION

The superposition of Figs. 3 and 4 shows that the two Arrhenius plots for 1-bromobutane and the one for 1-bromo-2-methylpropane intersect in the same region. This means that, as in many other rate processes, a compensation effect is operative, like that established by Schwab (10) for a given reaction on a series of catalysts:

$$\log A = b + aE \quad (3)$$

TABLE 3
RATE CONSTANTS FOR DEHYDROHALOGENATION OF 2-BROMOBUTANE ON 9.1% KBr/Al₂O₃,
AT VARIOUS TEMPERATURES (CATALYST No. 22B)

Temp (°C)	$k(=k_{trans} + k_{cis}) \times 10^3$ (min ⁻¹)			
	From <i>trans</i> -2-butene	From <i>cis</i> -2-butene	$k_{trans} \times 10^3$ (min ⁻¹)	$k_{cis} \times 10^3$ (min ⁻¹)
50.4	0.84 ± 0.02	0.92 ± 0.02	3.9	4.9
57.5	1.49 ± 0.01	1.55 ± 0.02	7.1	8.1
61.0	1.89 ± 0.03	1.91 ± 0.05	8.5	10.5
65.0	2.49 ± 0.05	2.57 ± 0.05	11.5	13.8
71.1	3.80 ± 0.08	4.0 ± 0.1	18	21
75.5	4.9 ± 0.2	5.0 ± 0.3	22	28
80.2	6.7 ± 0.3	7.0 ± 0.3	31	38

The same relation has also been found to hold for the dehydration of a series of alcohols, i.e., for a series of related reactions, on a single catalyst (11). Disregarding the reaction of 2-bromobutane for the moment, we are left in our case with only the three above mentioned reactions to verify Eq. (3). Although three points are generally inadequate for such a verification, the rather high accuracy of our results permits us to attempt a tentative interpretation of Eq. (3) in terms of the heat of adsorption of the reactant molecules. Figure 5 shows the plot of log A versus E , and also separate plots of each of these parameters (log A and E) versus $-\Delta H_{ad}$. All three plots are linear obeying the equations

$$\log A = -0.832 + 0.548E, \quad (4)$$

$$\log A = -2.61 + 1.42(-\Delta H_{ad}), \quad (5)$$

$$E = -3.24 + 2.59(-\Delta H_{ad}). \quad (6)$$

Clearly by combining Eqs. (5) and (6) we obtain $\log A = -0.834 + 0.548E$ in agreement with Eq. (4).

From the above, one is inclined to believe that the values of the Arrhenius parameters are somehow governed by the value of the heat of adsorption. If this correlation is not purely fortuitous, certain conclusions can be drawn about the mechanism of the dehydrobromination reactions. First of all, it must be recalled that the values of E determined in this study are true activation energies for the surface reactions and not apparent ones. In the extreme case that a change in the heat of adsorption of the reactant is not accompanied by a change in the heat content of the transition state, an increase in the enthalpy of activation, and hence in the Arrhenius activation energy, equal to the change in the heat of adsorption would be expected. This obviously represents an

TABLE 4
ACTIVATION ENERGIES (E), FREQUENCY FACTORS (A) AND HEATS OF ADSORPTION (ΔH_{ad}) FOR
DEHYDROHALOGENATION REACTIONS OF BROMOBUTANES ON 9.1% KBr/Al₂O₃ CATALYSTS,
TOGETHER WITH SURFACE AREAS AND PORE VOLUMES OF THE LATTER

Catalyst no.	Surface area (m ² g ⁻¹)	Pore vol (ml g ⁻¹)	Reactant	ΔH_{ad} (kcal mole ⁻¹)	E (kcal mole ⁻¹)	log A
21A	—	—	1-Bromobutane	-8.90	19.98	10.13
22A	86.0	0.202	1-Bromobutane	-10.28	23.40	12.00
22E	86.7	0.255	1-Bromo-2-methylpropane	-8.76	19.34	9.77
22B	88.7	0.200	2-Bromobutane ^a	—	15.46	8.05
22B	88.7	0.200	2-Bromobutane ^b	—	15.66	8.26

^a For conversion to *trans*-2-butene.

^b For conversion to *cis*-2-butene.

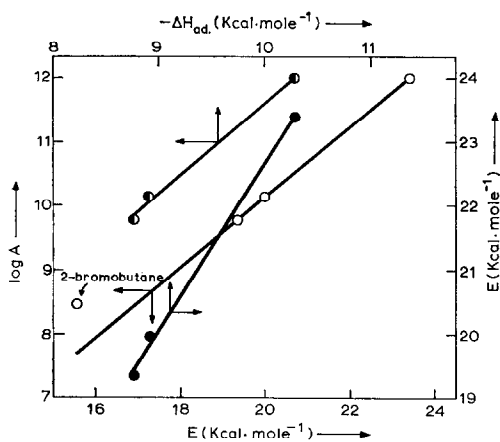


FIG. 5. Compensation effect in the dehydrohalogenation of 1-bromobutane and 1-bromo-2-methylpropane.

upper limit in the activation energy change. However, Eq. (6) shows that an increase of $-\Delta H_{ad}$ by 1 unit causes an activation energy increase by 2.6 units and this result seems unintelligible. One may argue that this number is unreliable, since it comes from a maximum difference between heats of adsorption of $10.28 - 8.76 = 1.52$ kcal mole⁻¹. It is also true that Eq. (6) is established with only three points and for this reason we consider the present interpretation only a tentative one. However, the error in the highest and the lowest heat of adsorption given above is 0.10 and 0.31 kcal mole⁻¹, respectively, and these errors are quite small. A statistical test of significance shows that the difference of 1.52 kcal mole⁻¹ is highly significant at the 5% probability level. The 95% confidence limits of this difference are 1.52 ± 0.95 , and the slope of Eq. (6), which would have been calculated from the upper (2.47) and the lower (0.57) of these limits, is 1.6 and 7.1, respectively. This shows that 1 unit increase in $-\Delta H_{ad}$ would be accompanied by at least 1.6 units increase in the activation energy. Therefore the number 2.6 found as the slope of Eq. (6) is not altogether unreliable.

Similarly, since surface adsorption is normally a spontaneous and entropy decreasing process, the term $T\Delta S_{ad}$ cannot be greater in magnitude than ΔH_{ad} , and at the most would be equal to the latter under

equilibrium conditions. Thus an upper limit of $\partial(\log A)/\partial(-\Delta H_{ad})$ equal to $1/(2.303 RT)$ is expected. At 400°K this factor equals 0.55, while Eq. (5) gives 1.42, i.e., a factor 2.6 times greater.

The above considerations lead to the conclusion that probably the rate determining step is not the passage of the reactant directly to products, but the decomposition of an intermediate which is adsorbed on the surface at least 2.6 times stronger than the original reactant. Thus the heat of adsorption of this intermediate is proportional, but not equal, to the measured heat of adsorption. The lower limit of the first heat is of the order of $9 \times 2.6 \approx 23$ kcal mole⁻¹, and this places the interaction with the surface in the domain of chemisorption. The strength of the interaction suggests that the postulated intermediate is a charged species, possibly a carbonium ion or a carbanion. This leads us to a two-step mechanism, the second step being rate determining, which is also consistent with two other experimental facts: (a) all four possible butenes are produced from 1-bromobutane, 2-methylpropene requiring a skeletal rearrangement, and (b) the ratio of *cis*- to *trans*-2-butene produced from 2-bromobutane is not substantially different from unity (1.20 to 1.27) and this ratio does not change appreciably with temperature (cf. activation energies of 2-bromobutane in Table 4). A concerted *E2*-like mechanism, such as that occurring in the liquid phase, would favor the *trans* product and indeed this has been found (12) in the decomposition of 2-bromobutane, which gives the *trans*-2-olefin at a rate six times that of the *cis*-isomer.

Using the Arrhenius parameters of Table 4, we calculated the overall rate constant for the dehydrobromination of 2-bromobutane at 120°C. This is 0.637 min⁻¹, and can be compared with the rate constants of 1-bromobutane (Table 1) at 119.3°C (0.1149 min⁻¹), and at 119.0°C (0.117 min⁻¹) or with that of 1-bromo-2-methylpropane (Table 2) at 121.3°C (0.1159 min⁻¹). It is seen that the reaction of 2-bromobutane is 5.5 times faster than those of the other two bromides. This

means a lower free energy of activation by 1.33 kcal mole⁻¹ in the 2-bromobutane; this is probably due to a better stabilization of the transition state in this reactant. One therefore could not expect the Arrhenius parameters in this case to obey Eq. (4), although a compensation effect in the general sense is observed (cf. Fig. 5). There is practically no difference in the free energy of activation between the three reactions from which Eq. (4) has been derived.

A comparison of the structures of the three bromides studied in this paper shows that the difference between 1-bromobutane and 1-bromo-2-methylpropane is virtually equivalent to a substitution of a β -hydrogen by a methyl group in the second reactant. This will influence the acidity of the remaining β -hydrogen atom, but since no difference in the rate of dehydrobromination between these two bromides is observed, we can conclude that the hydrogen separation does not occur in the rate determining step. Comparing now 1-bromobutane with 2-bromobutane we see that their difference amounts approximately to a substitution of an α -hydrogen by a methyl group, and the rate is increased about fivefold, as has been mentioned. This difference is of course small compared with the much greater differences caused by α -methylation in the gas phase, where it is believed that C α -Br breakage dominates the transition state (13). Nevertheless, we have an indication that the bromide is probably removed in the rate determining step. This being the second step, as mentioned earlier, rather excludes the possibility that a carbonium ion is formed as an intermediate, since the formation of such an ion would occur in the first step of the reaction. The most plausible possibility which is left is the fast removal of a proton in the first step, followed by a slow decomposition of the intermediately formed carbanion to yield the olefin. Proton removal can be facilitated by interaction with the oxide ions of the alumina surface and stabilization of the formed carbanion is possibly brought about by interaction with aluminum ions of the sur-

face. Thus, although a carbanion is generally very reactive in solution, it can be stabilized on a catalyst surface, so that its decomposition to form olefin and bromide ion can become sufficiently slow. In the case that the rate of the last process is much slower than the readdition of a proton to form the original molecule, i.e., the reverse of proton abstraction, the first step can be considered in equilibrium. This type of mechanism is closely analogous to the *E1cB* mechanism in the liquid phase (13, p. 78). Of course, such a mechanism is in disagreement with what is generally known in the literature, since in most cases investigated the mechanisms are *E1* and *E2*. However, evidence in the direction of an *E1cB* mechanism has been reported (14). It has also been recognized (1) that "this mechanism should occur in systems with strong anion-H interaction and weak cation-X interaction." This is consistent with the argument presented above.

According to Lane, Lane and Phillips (11) the function of the modifier (KBr) is to cover very active sites of the catalytic surface. In the present study there was no evidence for two different catalytic sites, as was postulated by Lane, Lane and Phillips (11) in order to explain the observance of two independent first-order reactions in the dehydration of alcohols over alumina modified with potassium chloride. The kinetics of the reaction in our case was always simple first-order. This disagreement is most probably due to the fact that we have used a different type of alumina than that used by the above authors.

CONCLUSION

The main purpose of the whole discussion in this paper was not to draw a definite conclusion about the mechanism of the reactions being *E1cB*, but to show: (a) that a correlation between adsorption data and Arrhenius parameters can lead to an interpretation of Eq. (3), and (b) that this correlation can provide a diagnostic criterion for a two-step mechanism in which the second step is rate determining. Whether this second step is the removal

of a halide ion or a proton is of secondary and specific importance only. It must be decided in each case on the basis of structural considerations, specific interactions with the surface, and other factors. The part of the discussion concerning this latter point was meant as a trial example only.

Other experiments are under way to explore further the potentialities of the above-mentioned correlation.

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