data at 300 and 200°K. indicates an escape yield of only 5×10^{-4} at 77°K. This is a further argument in favor of the conclusion that the R and X⁻ species formed in the present work are trapped in the same solvent envelope.

Radical Production by Photodissociation of Alkyl Iodides in 3-MP at 77°K. Methyl iodide and ethyl iodide at 0.005 mole fraction in 3-MP glass at 77°K. were each photolyzed for 4 min. with the unfiltered radiation of the Hg lamp. The former produced the sharp four-line spectrum characteristic of methyl radicals, which decayed with a half-life similar to that for CH_3 radicals produced by the photoionization process and discussed above. Two additional lines outside the methyl lines did not decay as rapidly and, when the methyl signal had disappeared, proved to be part of a 3-methylpentyl radical spectrum. This 3-methylpentyl radical spectrum was similar to that produced[27] by the attack on 3-MP of hot H atoms from

the photolysis of HI. It is attributed to the abstraction of hydrogen from 3-MP by hot methyl radicals formed by the photolysis of CH_3I. Hot reactions of methyl radicals from the photolysis of gaseous CH_3I[28a] and of CH_3I in liquid cyclohexane,[28b] in alkene glasses at 77°K.[28c] and in inert gas matrices at 20°K.,[28d] have been demonstrated earlier. The spectrum from the photolysis of C_2H_5I in 3-MP has six lines with intensity ratios which are characteristic of both ethyl[17] and 3-methylpentyl[27] radicals. The line splittings are *ca.* 24 gauss, slightly less than those observed for ethyl (*ca.* 27 gauss). These splittings and the detailed shape of specific lines are characteristic of the 3-MP radical, suggesting a high efficiency of H abstraction by hot ethyl radicals from the photolysis of C_2H_5I in this system.

(27) S. Aditya and J. E. Willard, *J. Am. Chem. Soc.*, in press.

(28) (a) G. M. Harris and J. E. Willard, *ibid.*, 76, 4678 (1954); (b) R. F. Pottie, W. H. Hamill, and R. R. Williams, Jr., *ibid.*, 80, 4224 (1958); (c) P. B. Ayscough and H. E. Evans, *Trans. Faraday Soc.*, 60, 801 (1964); (d) C. D. Bass and G. C. Pimental, *J. Am. Chem. Soc.*, 83, 3754 (1961).

The Hydrogen Bromide Catalyzed Isomerization of *n*-Butenes. II.[1] Kinetic Investigation

Allan Maccoll and R. A. Ross

Contribution from the William Ramsay and Ralph Forster Laboratories, University College, London, England. Received June 15, 1965

The kinetics of the hydrogen bromide catalyzed isomerization of butene-1 to butene-2 has been studied in a static system over the temperature range 559–656°K. The reaction is predominantly homogeneous and molecular with the kinetic form: rate of isomerization of butene-1 = k_2[butene-1][HBr]. The Arrhenius equation over this temperature range is log k_2 = 11.86 − 26,300/ 2.3RT, where k_2 is in units of mole⁻¹ cc. sec.⁻¹.

Introduction

Hydrogen bromide is known to catalyze the dehydration of alcohols in the gas phase and these reactions have been claimed to be molecular.[2] As one guide to mechanism in these reactions the olefin distribution from unsymmetrical alcohols has been investigated. In the case of *t*-pentyl alcohol the equilibrium proportions of the three methylbutenes were found,[3] clearly indicating isomerization of the olefins by hydrogen bromide. The equilibrium proportions of the *n*-butenes were found as the products from *sec*-butyl alcohol and hydrogen bromide,[2] again suggesting isomerization.

The olefin distribution found in the dehydrobromination of *sec*-butyl bromide also indicated isomerization by the halide formed.[4] Hydrogen bromide has been

shown to catalyze the isomerization of cyclopropane,[5] the kinetic behavior being similar to that found in the catalyzed alcohol dehydrations. The catalyzed isomerization of *n*-butene by hydrogen bromide is now reported.

Experimental Section

The materials and apparatus have been described previously.[1] The Pyrex reaction vessel was "conditioned" by allowing a mixture of butenes to remain in it for a few days at ~450°. This resulted in a transparent, amber-colored coating being deposited uniformly on the surface. Air was rigorously excluded from the apparatus and a small amount of reaction mixture was generally left in the vessel between runs and overnight, the vessel only being fully evacuated just prior to the start of a run. Taps on the vacuum line were greased with Apiezon M grease except those that came in contact with reaction products, which were greased with B.D.H. Fluorube A grease.

Procedure. Butene-1 was normally admitted to the reaction vessel first and its pressure measured (no detectable reaction occurs below ~450°). Hydrogen bromide was admitted from a much higher pressure at zero time. Any temperatue change, measured with a glass-covered thermocouple probe inside the reaction vessel, is less than 0.2°.

At the end of a run the products were expanded into an evacuated 5-l. flask containing 10 g. of $Ba(OH)_2$[5]

(1) Part I: A. Maccoll and R. A. Ross, *J. Am. Chem. Soc.*, 87, 1169 (1965).

(2) See, *e.g.*, R. L. Failes and V. R. Stimson, *J. Chem. Soc.*, 653 (1962), and previous papers in the series.

(3) V. R. Stimson and E. J. Watson, *ibid.*, 3920 (1960).

(4) A. Maccoll and R. H. Stone, *ibid.*, 2756 (1961).
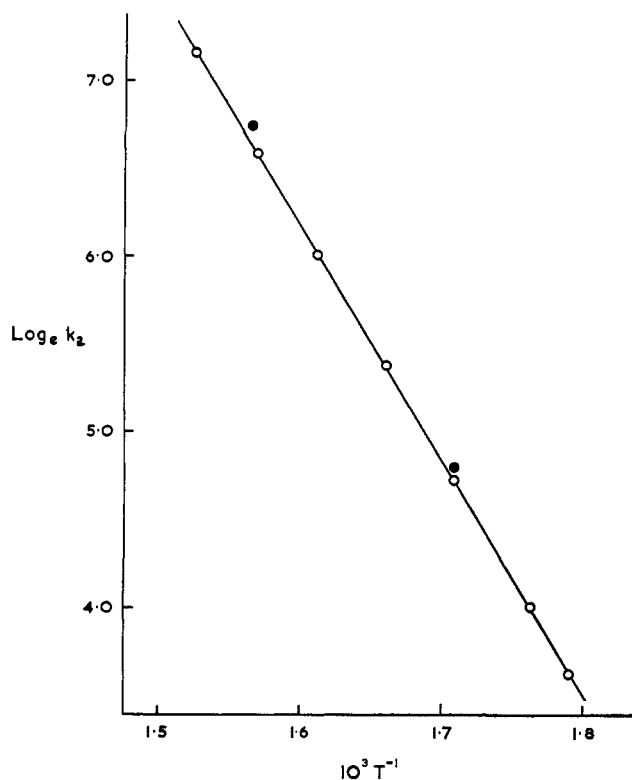
(5) R. A. Ross and V. R. Stimson, *ibid.*, 1602 (1962).

Figure 1. Arrhenius plot for the reaction butene-1 + HBr → butene-2 + HBr; rate = k_2[butene-1][HBr] (k_2 in mole^{-1} cc. sec.$^{-1}$).

and then pumped into a trap at $-180°$ before being distilled from $-50°$ into a tap vessel. The resultant butene mixture was thoroughly mixed with a pinpoint flame before being sampled for the vapor phase chromatography (v.p.c.) apparatus described in part I.[1] At least three samples from each mixture were run on the v.p.c. and in general these samples agreed to within $\pm 2\%$.

Admitting the reagents in the reverse order to that described above had no effect on the results. "Zero" ($\sim$5 sec.) time runs showed no isomerization starting with any of the n-butenes, thus indicating the "inert" nature of the sampling procedure.

Results

The results were treated[6] as a first-order approach to equilibrium in the system
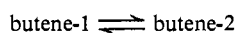
$$\text{butene-1} \rightleftharpoons \text{butene-2}$$

$$(k_1 + k_{-1}) = \frac{1}{t} \ln \frac{B_{2e}}{B_{1t} - B_{1e}} \tag{1}$$

where $B_{2e} = \%$ butene-2 at equilibrium, $B_{1t} = \%$ butene-1 at time t, and $B_{1e} = \%$ butene-1 at equilibrium. The composite first-order constant ($k_1 + k_{-1}$) obtained was divided by the hydrogen bromide pressure and combined with the appropriate equilibrium constant given by

$$\log K_{1,2} = 623T^{-1} - 0.459$$

as derived in part I,[1] thus giving k_2, the second-order specific rate of disappearance of butene-1.

(6) A. A. Frost and R. G. Pearson, "Kinetics and Mechanisms," John Wiley and Sons, Inc., New York, N. Y., 1953, pp. 172, 173.

$$\text{butene-1} + \text{HBr} \longrightarrow \text{butene-2} + \text{HBr}$$
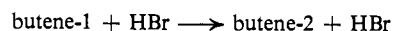
$$\text{rate} = k_2[\text{butene-1}][\text{HBr}] \tag{2}$$

The method used by Benson, et al.,[7] to treat their data in the iodine catalyzed isomerization of n-butenes is equivalent to that described above.

The reaction proceeded without any pressure change, and analyses at different times with nearly identical reaction mixtures showed that the specific rate was constant to 90% reaction (using equilibrium as 100% reaction) (Table I).

Table I. Rate Constants and *trans/cis* Ratios at Increasing Percentage Reaction (585.3°K.)

Butene-1[a]	% reaction[b]	$10^4 k_2$[c]	*trans/cis*
78.6	26.7	20.0	1.36
66.9	41.3	21.4	1.36
63.5	44.3	23.2	1.37
55.6	55.5	21.7	1.29
43.4	70.7	21.1	1.25
27.5	90.5	22.0	1.19
19.9	100.0	..	1.18

[a] % in product. [b] Equilibrium (19.9% butene-1) ≡ 100% reaction. [c] Actually ($k_2 + k_{-2}$) in min.$^{-1}$ cm.$^{-1}$; mean of 37 runs at this temperature, 23.3 ± 1.8.

Analysis of products showed that total n-butenes were constant throughout a run, as was hydrogen bromide. The order in butene-1 was confirmed by the constancy of the specific rate for different initial butene-1 pressures (53–220 mm.). The first-order specific rate was shown to be proportional to hydrogen bromide pressure over the range 49–270 mm. (Table II).

Table II. Variation of First-Order Specific Rate with HBr Pressure

HBr, mm.	$10^3 k_1$, min.$^{-1}$ [a]	$10^5 k_1$/HBr, min.$^{-1}$ mm.$^{-1}$ [b]
39	11.4	23.3
67	15.4	23.0
80	16.2	20.3
99.5	23.2	23.3
132	30.6	23.2
150	31.1	20.8
165	39.5	23.9
187	37.6	20.1
234	54.2	23.2
270	68.9	25.5

[a] Actually ($k_1 + k_{-1}$). [b] Mean of 37 runs, 23.3 ± 1.8.

Rates of experiments performed in a reaction vessel packed with concentric Pyrex tubes to increase the surface-to-volume ratio by a factor of six over the normal vessel at 585.3 and 639.5°K. gave mean values of $10^5(k_2 + k_{-2})$ 25.1 ± 0.8 and 184 ± 12 min.$^{-1}$ mm.$^{-1}$. These are just outside the experimental scatter, higher than rates in the unpacked vessel (23.3 ± 1.8 and 150 (calcd.)), and are marked with solid points in Figure 1, confirming that the reaction is predominantly homogeneous.

(7) S. W. Benson, A. N. Bose, and P. Nangia, *J. Am. Chem. Soc.*, 85, 1388 (1963).

Cyclohexene is an efficient inhibitor in those alkyl bromide eliminations that have been claimed to proceed by bromine atom chains[8] and would be expected to be at least five times as efficient as n-butene,[8a] an expectation confirmed by its successful use in inhibiting chains in n-butyl bromide[8b] and sec-butyl bromide.[8b] Addition of up to 50 mm. of cyclohexene did not decrease the rate.

Cyclohexene (25, 48, 50, and 50 mm.) added at 585.3°K. gave values of 10^5k_2 of 20.3, 23.1, 22.0, and 24.2 min.$^{-1}$ mm.$^{-1}$, respectively, compared with 23.3 ± 1.8 as the mean of 37 runs without cyclohexene at that temperature.

Experimental scatter of the values for specific rate constants was somewhat larger ($\sim\pm10\%$) than for normal kinetic work, but each rate is only determined at one point so the results are, in fact, not much more scattered than would be expected. The error in k_2 at each temperature is about ±7%. The variation of rate with temperature is shown in Figure 1, the least-squares straight line giving the Arrhenius equation

$$\log k_2 = 11.86 - 26{,}300/2.3RT$$

with k in mole^{-1} cc. sec.$^{-1}$.

Results for runs at increasing percentage reaction show (Table I) that trans-butene-2 is formed initially in amounts greater than the equilibrium proportion. The mean specific rates (k_2), percentage errors, and the number of runs performed at each temperature are shown in Table III, along with sample runs at each temperature.

Table III. Variation of Rate with Temperature and Sample Runs

Temp., °K.	p_{HBr}, mm.	p_B,[a] mm.	t, min.	%B$_t$[b]	k_2, cc. mole^{-1} sec.$^{-1}$	% error in k
585.6	142.2	130.9	60	59.9	38	10?
567.3	160.5	100.0	45	53.4	57.0	
	135.5	204.0	53	54.6	55.0	
		Mean of 9 runs			55.5	6
585.3	168.5	165.0	8	78.7	112	
	168.0	173.0	20	55.9	116	
	157.0	178.5	35	43.4	109	
	160.0	166.5	60	27.5	120	
		Mean of 37 runs			114	7
602.3	150.0	127.0	12	57.1	216	
	144.0	137.0	13	54.7	226	
		Mean of 11 runs			218	6
620.7	109.5	186.5	10	54.9	397	
	93.0	112.0	10	57.6	423	
		Mean of 7 runs			408	5
637.7	77.0	132.0	8	53.1	756	
	85.0	97.0	7	56.7	710	
		Mean of 20 runs			720	6
656.2	83.0	130.5	5	51.6	1280	
		Mean of 3 runs			1290	7

[a] Initial pressure of butene-1. [b] (Butene-1/total butenes) × 100 at time t.

As noted by Ogasawara and Cvetanović,[9] it is difficult to obtain reliable kinetic results starting from butene-2 because of the small percentage of butene-1

(8) (a) A. Maccoll and P. J. Thomas, J. Chem. Soc., 5033 (1957); (b) M. N. Kale, A. Maccoll, and P. J. Thomas, ibid., 3016 (1958).
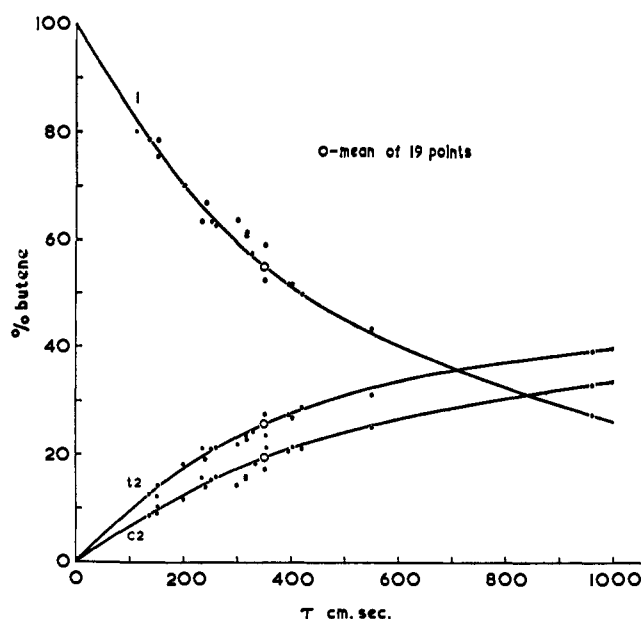(9) S. Ogasawara and R. J. Cvetanović, J. Catalysis, 2, 45 (1963).

Figure 2.

present at equilibrium, but one run starting from trans-butene-2 (638°K.) gave $(k_2 + k_{-2}) = 160 \times 10^{-4}$ min.$^{-1}$ cm.$^{-1}$ in reasonable agreement with the value obtained starting from butene-1 (142 × 10^{-4} min.$^{-1}$ cm.$^{-1}$).

The results obtained at 585.3°K. are plotted in Figure 2 as mole fraction of butenes at different values of the time parameter τ (in min.$^{-1}$ cm.$^{-1}$), where τ is the product of the time of the run and the pressure of hydrogen bromide used. These results were fitted to equations of the form

$$A = a_1 \exp(b_1\tau) + a_2 \exp(b_2\tau) + a_3 \exp(b_3\tau)$$

(where A is the mole fraction of the butene, and a and b are functions of the six rate constants) by a least-squares procedure on a Ferranti Pegasus computer.

The procedure used improved rate constants estimated from the curves in Figure 2. The final rate constants obtained result in a curve for butene-1 that has a maximum deviation from the experimental results of 6.9% and an average deviation of 2.3%. These rate constants are shown in Table IV, with the nomenclature explained by the following scheme.
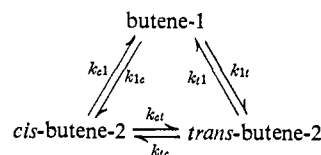
From these results an independent determination of the equilibrium constants at this temperature can be obtained and these agree satisfactorily with the experi-

Table IV. Rate Constants at 585.3°K.[a]

k_{1t}	k_{1c}	k_{t1}	k_{c1}	k_{ct}	k_{tc}
72.2	41.8	32.8	22.4	280	238

[a] Values of k in mole^{-1} cc. sec.$^{-1}$.

Table V. Equilibrium Constants at 585.3°K.

	K_{1t}	K_{1c}	K_{ct}
From k values	2.20	1.87	1.18
Part I	2.18	1.84	1.18

mentally determined equilibrium constants from part I[1] (Table V).

The range of values of τ obtained at other temperatures did not allow a reasonable determination of the six rate constants. However the k_{1t} and k_{1c} values obtained at 602.3 and 637.7°K. as well as those at 585.3°K. are compared with the k_2 values (calculated by eq. 1 and 2) in Table VI., where agreement is satisfactory and justifies the use of k_2.

Table VI[a]

Temp., °K.	k_{1t}	k_{1c}	$k_{1t} + k_{1c}$	k_2
585.3	72.2	41.8	114	114
602.3	141	74	215	218
637.7	448	240	688	720

[a] Values of k in mole^{-1} cc. sec.$^{-1}$.

The six rate constants involved in the isomerization of n-butenes over alumina have recently been determined in a novel manner using a "hydrostatic simulator."[10]

Discussion

The absence of any pressure change, the lack of effect of 50 mm. of cyclohexene, and the fact that the total amount of n-butene was constant throughout a run (as was the amount of hydrogen bromide) convince us that the reaction is molecular.

A reaction path via sec-butyl bromide

$$\text{butene-1} + \text{HBr} \xrightarrow{a} \text{sec-BuBr} \xrightarrow{b} \text{butene-2} + \text{HBr}$$

would only be possible if the amount of sec-butyl bromide present were very small ($\leqslant 1$ mm. pressure), otherwise this material would have been detected by v.p.c. and a pressure drop would have been observed. Further the rate of elimination of sec-butyl bromide has been determined[8b,11] and if the highest of the literature rates[11a] is combined with Maccoll and Stone's estimate[4] of the product distribution, a value for k_b in the above scheme can be obtained. At 620°K. $k_b = 1.02 \times 10^{-3}$ sec.$^{-1}$. If the equilibrium constant for the elimination can also be estimated, a value can be obtained for k_a. The ratio of final-to-initial pressures in the elimination reaction (1.86) enables a lower limit to be placed on the equilibrium constant and a value of 1.6 atm. is obtained, but this will ignore the contri-

bution of dead space and polymerization to the final pressure. A further estimate can be made by extrapolating Lacher's[12] heat of hydrobromination data by Kirchoff's equation using C_p values quoted by Bjellerup[13] and taking the ΔS value to be approximately the same as Howlett found[14] for t-butyl bromide (similarly extrapolated). This leads to an equilibrium constant of 3.94 atm. at 620°K. (Howlett's data[14] would give K_p (t-BuBr $\rightleftharpoons$ isobutene $+$ HBr) $\sim$ 30 at 620°K.). This figure is still likely to be low but yields a value for k_a of 67 mole^{-1} cc. sec.$^{-1}$.

These values for k_a and k_b can now be used in an adaption of Chien's solution[15] of a similar system. At 620°K. after 10 min. (cf. Table III) starting with 100 mm. of both butene-1 and HBr, pressures of butene-1, sec-butyl bromide, and butene-2 would be 90.6, 3.3, and 1.3 mm. giving a k_2 value as calculated by (1), etc., of $\sim$10 mole^{-1} cc. sec.$^{-1}$ compared with 410 found. If, however, rates high enough to produce the over-all rate found are used, the pressure of sec-butyl bromide produced is $>$10 mm., so that a mechanism via sec-butyl bromide can be ruled out. A reaction path through a six-centered transition state
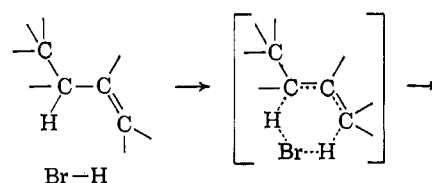
would seem possible and would also be consistent with the initial formation of trans-butene-2 being favored (cf. Table I).

Another possible mechanism would be similar to that suggested by Stimson[16] for the hydrogen halide catalyzed dehydrations of alcohols. That is a mechanism similar to the six-centered mechanism above, but with the C–H bond breaking playing no part in the rate-determining step which could then be thought of as a type of protonation. The information from the present investigation cannot differentiate between these two possibilities, although the value of the "A" factor suggests that the transition state is less rigid than might be expected for the six-centered mechanism and hence supports the "protonation" mechanism.

(10) D. Kallo and G. Schay, *Acta Chim. Acad. Sci. Hung.*, 39, 183 (1963).

(11) (a) A. Maccoll and P. J. Thomas, *J. Chem. Soc.*, 2445 (1955); (b) S. Sergeev, *Dokl. Akad. Nauk SSSR*, 106, 299 (1956).

(12) J. R. Lacher, T. J. Billings, D. E. Campion, K. R. Lea, and J. D. Park, *J. Am. Chem. Soc.*, 74, 5291 (1952).

(13) L. Bjellerup, *Acta Chem. Scand.*, 15, 121 (1961).

(14) K. E. Howlett, *J. Chem. Soc.*, 2834 (1957).

(15) J. Chien, *J. Am. Chem. Soc.*, 70, 2256 (1948).

(16) A. Maccoll and V. R. Stimson, *J. Chem. Soc.*, 2836 (1960).