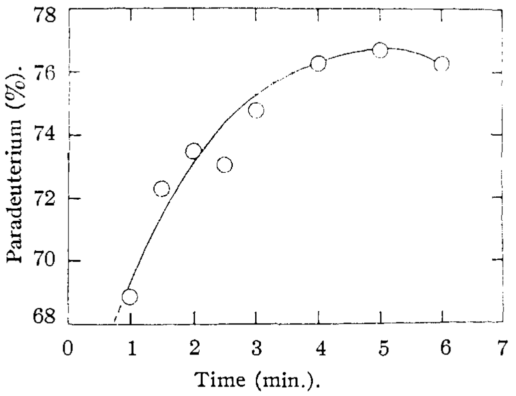

Fig. 5.—Double-stage separation of paradeuterium on alumina.

gram of alumina. The rate constant for the ortho–para conversion was found to be 3×10^{-7} mole per sec. per gram of alumina.[8] From this rate constant it is calculated that approximately one hour would be required to convert a static monomolecular layer of 100% orthohydrogen to 50% orthohydrogen. This rate of conversion would give a decrease in the orthohydrogen concentration of about 1% per minute; however it must be remembered that these experiments were not conducted under static conditions. Gas was continuously removed, and the gas phase would be richer in parahydrogen than the adsorbed layer. This fact, combined with the fact that the rate of ortho–para conversion is not negligibly small, accounts for the observed rise in ortho concentration until a maximum of approximately 99% is reached and then the decrease as the rate of ortho–para conversion becomes effective.

TABLE I

TRIPLE-STAGE SEPARATION OF ORTHOHYDROGEN

Time, min.	Vol. removed, cc. S.T.P.	Concn. of orthohydrogen, %
1	500	97.1
2	330	97.8
3	300	98.8
4	250	99.1
5	200	99.3
6	150	99.3
7	120	98.8
8	80	98.6

TABLE II

DOUBLE-STAGE SEPARATION OF PARADEUTERIUM

Time, min.	Vol. removed, cc. S.T.P.	Concn. of paradeuterium, %
1	500	68.9
1.5	500	72.3
2	500	73.5
2.5	500	73.1
3	350	74.8
4	350	76.3
5	300	76.7
6	200	76.3

Heating of alumina to bring about rapid desorption had no influence on the rate of ortho–para conversion, for it has been found that at these temperatures the rate of conversion is not temperature-dependent.[10] By increasing the number of adsorption–desorption stages paradeuterium or orthohydrogen of very high purity could be prepared by this method.

Acknowledgments.—The authors are grateful to Professor E. N. Lassettre for many helpful suggestions.

[10] E. Cremer and M. Polanyi, *Z. physik. Chem.*, **B21**, 459 (1933).

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[CONTRIBUTION FROM THE GIBBS CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

Rate of Thermal Isomerization of *cis*-Butene-2

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The rates of isomerization of gaseous *cis*- and *trans*-butenes-2 were investigated using infrared absorption as the analytical technique. The ratio of the rate constants agrees well with the elsewhere determined value of the equilibrium constant. The first-order rate constants of the *cis*-butene isomerization, which was studied in more detail, show pressure dependence and fit reasonably well to straight lines in plots of $1/k$ against $1/P$. The derived limiting rate constants, k_∞, are represented very well by the equation $k_\infty = 10^{11} \exp(-52{,}000/RT)$ sec.$^{-1}$. The observed frequency factor is close to those reported elsewhere for several other *cis–trans* isomerization reactions. The discrepancy between the presently determined value of the frequency factor for butene-2 and an earlier measurement of it is traced to a concurrent heterogeneous reaction which distorted earlier work.

In 1936 Kistiakowsky and Smith[1] described experiments on the rate of thermal isomerization of *cis*-butene-2, analyzing by the melting point depressions. This work led to the surprising results that the first-order frequency factor A apparently equalled 2 sec.$^{-1}$ and the energy of activation E = 18,000 cal./mole in the Arrhenius equation $k = Ae^{-E/RT}$. Consequently *cis-trans* isomerizations were divided into three classes, according to whether A and E were high, as expected from collision theory (*ca.* 10^{11} sec.$^{-1}$ and 45,000 cal., respectively), medium (10^5 and 26,000) or low, the last class being represented only by butene-2. The theoretical implications of this were discussed by Glasstone, Laidler and Eyring,[2] who offered an explanation for the middle group of isomerizations,

[1] G. B. Kistiakowsky and W. R. Smith, THIS JOURNAL, **58**, 766 (1936).

[2] S. Glasstone, K. L. Laidler and H. Eyring, "Theory of Rate Processes," McGraw-Hill Book Co., New York, N. Y., 1941.

based upon a postulated triplet state of an ethylenic molecule. However, the data for butene-2 remained hard to reconcile with collision theory, and Kistiakowsky and Smith proposed a chain mechanism for the reaction. Since 1936 the method of infrared spectroscopy has become available, the absence of which made the original work difficult and uncertain. Hence it was decided to reinvestigate the butene-2 isomerization by this newer method.

Experimental

The butene-2 isomers were obtained in pure form from the Phillips Petroleum Company. The reaction occurred in a 500-ml. carbonized Pyrex flask inside a well-stabilized electrically-heated furnace, operating from a Sola 1,000-watt constant voltage transformer. This arrangement kept temperature variations during the course of an experiment generally below ± 0.2°. Furnace temperature was measured by means of a platinum resistance thermometer, which could be read to ± 0.007°. The reaction flask was connected by a short length of narrow tubing and vacuum stopcock to a glass system, evacuated by a mercury diffusion pump and oil pump. The experimental procedure consisted of first evacuating the system to 10^{-5} mm., as read by a McLeod gauge. *cis*-(or *trans*)-butene-2 was then let into the reaction flask to a pressure of 200, 300 or 400 mm. as read on a mercury manometer and was allowed to isomerize for periods varying from 44 to 2427 minutes. At the end of an experiment, the reaction mixture was condensed out of the furnace into a U-tube with a Dry Ice–acetone mixture. After short pumping to remove non-condensable gases (and some butene vapors), the liquid was allowed to warm up and to vaporize into the infrared cell to a pressure of 150 mm. A 10 cm. long cell with NaCl windows and the double-beam Perkin-Elmer recording spectrometer were used. Since the temperature of a Dry Ice–acetone mixture (−78.5°) is *ca.* 80° below the boiling points of the butenes-2 and since *cis*- and *trans*-butene-2 boil only 2.8° apart, the error resulting from fractional distillation of the isomers is negligible. In fourteen experiments, the pressure of the reaction mixture was measured at the end of a run just before condensing, in order to determine whether there were any pressure changes during an experiment due to decomposition or polymerization.

Readings were made for *trans*-butene-2 at 10.71 μ and *cis*-butene-2 at 14.91 μ, transmission being read to ±0.1%. After each spectrum had been recorded, the gas cell was removed and the air line at 13.885 μ recorded to serve as a reference point. By taking spectra of prepared *cis*–*trans* mixtures of known composition, calibration curves were obtained for each isomer. Since the calibration points fell on the curves within ± 0.8%, it was possible to read off the composition of mixtures containing a small amount of *trans*-butene to ± 0.7% by the calibration curve at 10.71 μ, and mixtures with a small amount of *cis* to ±0.2% at 14.91 μ.

Experimental Results

The outcome of the experiments is presented in Table I, in the order in which they were run. Column 4 gives the change of pressure during an experiment, where measured, as per cent. of the initial pressure. A slight increase always was observed, on the average 1.5%. Column 6 is the first-order rate constant. Two series of runs were made at 417°, before and after the runs at the other two temperatures. Rate constants for the second series on the average are somewhat lower than those of the first series.

All the values were averaged together since the two sets overlapped and there was no reason for favoring one set over the other. In some of the infrared records there was a slight dip in transmission at 10.95 μ, where propane has an absorption band, suggesting a decomposition side-reaction. No other anomalous absorption bands were observed in any experiment.

TABLE I

Starting isomer, *cis*	Time (min.)	Initial pressure (mm.)	ΔP, %	% *trans*	$k \times 10^6$, sec.$^{-1}$
417°C.	487	396.0		14.4	5.3
	360	397.2		11.9	5.9
	242	395.9		8.3	6.0
	357	199.1		7.6	3.7
	537	201.8		9.6	3.1
	305	200.0		8.6	4.9
	441	199.7		11.4	4.6
443°	217	196.8		17.5	14.8
	110	200.9		11.3	18.1
	67	200.3		6.7	17.3
	52	295.3		5.5	18.5
	65	299.7		7.6	20.1
	177	299.2		16.5	17.0
	88	300.0		10.8	21.8
	135	299.0		15.0	20.2
	75	397.4		9.8	22.9
	44	397.2		6.3	24.6
	118	397.5		14.3	21.9
391.5°	2285	199.6	+3.2	9.9	0.76
	2011	199.1	3.5	6.6	.57
	2116	199.0	2.5	8.6	.72
	330	299.8		1.9	.96
	2427	299.1	2.3	13.7	1.01
	1829	297.8	1.1	7.7	0.74
	362	398.7		2.5	1.22
	742	399.1		5.1	1.24
	1197	400.8	0.4	5.7	0.82
	1600	398.1	0.6	6.8	0.74
417°	185	298.7	1.1	3.8	3.5
	497	300.0	1.3	10.6	3.8
	420	399.4	1.7	10.0	4.2
	296	399.4	0.4	7.8	4.6
	192	399.7	0.8	4.0	3.6
Starting isomer, *trans*				% *cis*	
417°	305	398.3	0.9	8.1	4.7
	300	399.2	1.0	8.1	4.7

Discussion of the Results

In order to make an Arrhenius plot of log *k* *vs.* $1/T$, it was necessary at each temperature to determine the value of *k* extrapolated to infinite pressure. This was obtained at any given temperature by averaging the values of *k* for a particular pressure, plotting $1/k$ *vs.* $1/P$, and reading off the value of $1/k_\infty$ at $1/P = 0$. At 391.5 and 443°, this involved fitting a straight line by least squares through three points (corresponding to $P = 200$, 300 and 400 mm.), while the series at 417° contained measurements at only two pressures. The resulting values of k_∞ are: at 443°, $k_\infty = 36 \times 10^{-6}$ sec.$^{-1}$; 417°, $k_\infty = 9.4 \times 10^{-6}$ sec.$^{-1}$; 391.5°, $k_\infty = 2.0 \times 10^{-6}$ sec.$^{-1}$.

Figure 1 shows log k_∞ plotted against $1/T$. It is exceedingly accidental that the three points lie so close to a straight line, considering the probable errors involved. From the slope it is found that $E = 52{,}000$, $A = 10^{11}$. Taking into account the probable errors in the values for k_∞, and estimating the errors graphically as shown, the following extreme values are obtained: $A = 10^8, 10^{15}$ and $E =$

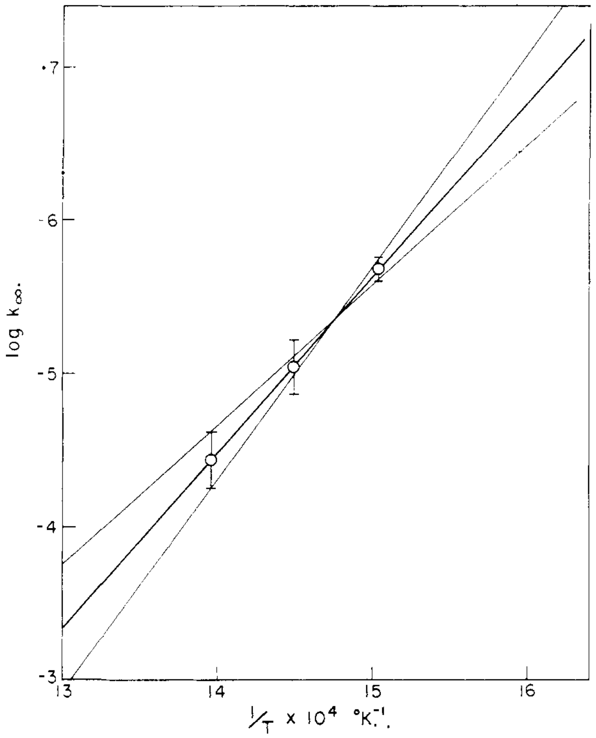

Fig. 1.—A plot of log k against $1/T$ with probable errors and extreme slopes indicated.

42,000, 62,000. The probable errors are, of course, much less. The 1936 value of the frequency factor ($10^{0.3}$) is completely outside the range of error. Furthermore, the values of A and E are relatively near those observed for methyl cinnamate,[3] stilbene,[4] cyanostyrene[5] and other normal *cis–trans* isomerizations of the high A–E class. The theoretical difficulties which the butene-2 isomerization formerly raised may thus be considered as eliminated.

Evidence that the rates observed for the conversion of *cis* to *trans* are substantially correct is provided by the data for the reverse reaction. Because *cis*-butene-2 is strongly absorbent at 14.91 μ, where *trans* hardly interferes at all, a small amount of *cis*-butene-2 being formed from *trans* can be detected easily. Hence our measurements for the *trans*-to-*cis* isomerization rate, 4.7×10^{-6} sec.$^{-1}$ at 417°, $P = 400$ mm., are probably accurate. The ratio of the reaction rates in opposite directions should be equal to the equilibrium constant for the reaction. One obtains $k_{\text{eq}} = (5.1 \times 10^{-6})/(4.7 \times 10^{-6}) = 1.1$, in excellent agreement with the value (1.12) obtained by direct analysis of the equilibrium mixture.

From the Lindemann–Hinshelwood theory, the rates of deactivation and decomposition of the activated molecule are equal at the pressure ($P_{1/2}$) where $1/k$ equals twice $1/k_\infty$. In our data, $P_{1/2}$ is 390 mm. at 391.5° and 230 mm. at 443°, the change with temperature not being significant because of experimental errors. The average value of $P_{1/2}$, 310 mm., implies that the activated butene-2 molecule has a lifetime of 9×10^{-10} second.

The question arises, why should earlier published results, derived from analyses by mixed melting points, have given an abnormally low value of A? The results of the 1936 study are in fair agreement with ours at 417°, but at 391.5°, the lowest temperature, the rates by melting points are almost four times as great as the infrared data. Unlike infrared spectroscopy, melting point depressions fail to distinguish between a geometrical isomer and any other reaction product. The occasional appearance of a propane band and the slight increase of pressure observed during the course of experiments make it clear that the thermal isomerization of butene-2 is accompanied by a decomposition side-reaction, which would have caused the 1936 study to yield too high rate constants. In addition, ΔP percentagewise is greater at lower temperatures and pressures, *i.e.*, in the longer experiments, suggesting that the side-reaction is less dependent on temperature and pressure. Hence the decomposition to propane was almost certainly a surface reaction on the wall of the flask and not cracking in the gas phase. The overestimation of the rate constants at 391.5°, caused by the inability of mixed melting points to discriminate between isomerization and side-reaction, led to a low temperature coefficient, hence to the low energy of activation and frequency factor reported in 1936.

Within the rather large experimental errors the data here presented give straight line plots of $1/k$ against $1/P$ in accord with the Lindemann–Hinshelwood theory of unimolecular reactions. It is interesting to note how short is the lifetime of this relatively complex molecule upon activation.

The authors wish to express their gratitude for the very great assistance rendered on many occasions by Dr. G. B. Kistiakowsky, Dr. Richard Williams and Dr. William Klemperer.

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[3] G. B. Kistiakowsky and W. R. Smith, THIS JOURNAL, **57**, 269 (1935).

[4] G. B. Kistiakowsky and W. R. Smith, *ibid.*, **56**, 638 (1934).

[5] G. B. Kistiakowsky and W. R. Smith, *ibid.*, **58**, 2428 (1936).