5. The electromotive force of transfer of the acid at unit activity from one solvent to another has been discussed in relation to the Born theory, and values of the sum of the reciprocals of the ionic radii have been evaluated from the electromotive force data.

6. Equations and their parameters are given by means of which the relative partial molal heat content and specific heat of the acid in the 10% and 20% methanol–water mixtures may be computed.

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[Contribution from the Chemical Laboratory of Harvard University]

# Kinetics of Thermal Cis–Trans Isomerizations. V

By G. B. Kistiakowsky and Walter R. Smith

In a continuation of previously reported studies on the rate of *cis–trans* isomerizations,[1,2,3,4] isomers of butene-2, which have recently become available in this Laboratory,[5] were selected for investigation. The equilibrium between the isomers has also been studied. Todd and Parks[6] have determined their entropies at room temperature, while the data of Kistiakowsky *et al.*,[5] give the heat of isomerization. As all these measurements have been made on identical samples, the results should form a consistent picture.

## Experimental Details

The butene-2 isomers were prepared by dehydration of secondary butyl alcohol with concentrated sulfuric acid at a temperature not far from 100°. They were purified by distillation as described elsewhere.[5]

The apparatus consisted of the usual static arrangement, a Pyrex flask in an aluminum block furnace, manually controlled. The gas pressure was read with the aid of a quartz spiral manometer and the flask was connected to the rest of the apparatus through a metal valve. The reaction was followed by determining the melting temperature of the reaction mixture. Pure butene-2 *cis* melts at $-139.3°$[5] and pure *trans* at $-105.8°$.[5] The melting points of several known mixtures were determined and a curve constructed. A eutectic is formed which melts at $-143.0°$ and contains 15.8% of the *trans* isomer. The melting points were determined in a cell which was sealed directly into the line. It consisted of a jacketed 10-mm. tubing, the interspace of which could be either evacuated or filled with air for a more rapid heat exchange. Around the outside of the inner tubing a few turns of fine platinum wire were wrapped. A long capillary mounted centrally within the inner tube through a ring seal at the top served as a thermocouple well for a very fine Cu–Constantan couple. A small soft iron band wrapped around the upper portion of the capillary in conjunction with an outside electromagnet actuated by interrupted current served to set the capillary in oscillatory motion providing efficient stirring of the sample. The lower portion of the cell was immersed in an unsilvered Dewar cylinder filled with filtered liquid air. A fine pencil of light was focused on the sample. After the hydrocarbon was condensed and frozen in the cell, the interspace was evacuated and a current passed through the heater sufficient to produce a slow melting rate. The temperature at which the last crystals of the solid disappeared was observed. It could be reproduced to somewhat better than 0.1°, which corresponds to about 0.5% accuracy in determining the composition of the mixture. This procedure was found to be considerably more accurate than a determination of the freezing temperature.

## Experimental Results

The pressure in all runs at both temperatures studied remained constant to $\pm 1$ mm. In all cases the condensed reaction mixture was colorless. The possibility of a balanced polymerization and decomposition appeared very slight since it is very unlikely that both reactions possess the same activation energy.

Sickman and Rice[7] have found that the polymerization of ethylene is greatly accelerated by free methyl radicals. Similar experiments per-

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(1) Kistiakowsky and Nelles, *Z. physik. Chem.*, **152**, 369 (1931).

(2) Nelles and Kistiakowsky, This Journal, **54**, 2208 (1932).

(3) Kistiakowsky and Smith, *ibid.*, **56**, 638 (1934).

(4) Kistiakowsky and Smith, *ibid.*, **57**, 269 (1935).

(5) Kistiakowsky, Ruhoff, Smith and Vaughan, *ibid.*, **57**, 876 (1935).

(6) Todd and Parks, *ibid.*, **58**, 134 (1936).

(7) Sickman and Rice, *ibid.*, **57**, 1384 (1935).

formed jointly with Dr. Sickman on our samples of butene-2 showed no polymerization, thus confirming the conclusion that butene-2 does not polymerize nearly as readily as ethylene. In the two runs reported at 1400 mm., however, it cannot be denied that polymerization may have added to the complexity of the reaction. The only other reaction which might obscure the *cis–trans* isomerization is the formation of butene-1. To test this possibility a eutectic mixture at 104 mm. was placed in the reaction flask and heated for 256 minutes at 691.4°K. If butene-1 is formed, the melting temperature should be lowered. Instead a rise was observed, giving the composition of the mixture as 18% *trans* compound. From this a reaction rate constant is calculated which agrees substantially with those obtained using pure *cis* isomer as the starting material. In two other instances, after taking the melting temperature of the reaction mixture, a measured amount of *trans* compound was added to bring the mixture past the eutectic composition and to give a melting temperature higher than the original. As the observed temperatures agreed with those calculated under the assumption that before addition only the butenes-2 were present, it is evident that the formation of butene-1 can be neglected under the conditions of the present experiments and that the reaction is exclusively the *cis–trans* isomerization. This is substantially in agreement with the findings of Hurd and Goldsby[8] who noted that even at 615° the formation of butene-1 is rather slow.

The results obtained in kinetic studies are presented in Table I. The velocity constants are calculated for a first order reaction, allowing for an equilibrium constant equal to 1.12 (see later). Because of the slowness of the reaction at still lower temperatures and of appreciable decomposition at higher ones, only a small temperature range could be covered. A considerable number of experiments were made at pressures above atmospheric but the results were quite erratic. The two sample experiments given in Table I indicate that the trend of velocity constants with pressure evident from low pressure runs is apparently not maintained. Three runs made with a packed flask indicate that the reaction is essentially homogeneous.

TABLE I

| Temp., °K. | Time, min. | Pressure, mm. | % *Trans* | $k_{\text{sec.}^{-1}}$ |
|---|---|---|---|---|
| 690 | 272 | 101 | 2.6 | $1.6 \times 10^{-6}$ |
| 692 | 324 | 101 | 3.2 | 1.7 |
| 691 | 338 | 103 | 3.4 | 1.7 |
| 692 | 131 | 202 | 2.1 | 2.7 |
| 691 | 235 | 206 | 4.0 | 2.9 |
| 693 | 262 | 204 | 4.8 | 3.1 |
| 691 | 193 | 400 | 7.0 | 6.4 |
| 691 | 240 | 403 | 9.0 | 6.8 |
| 689 | 320 | 402 | 11.8 | 6.9 |
| 664[a] | 342 | 104 | 4.0 | 1.8 |
| 663 | 440 | 102 | 3.5 | 1.4 |
| 663 | 444 | 105 | 2.6 | 1.0 |
| 663 | 712 | 103 | 4.3 | 1.0 |
| 664[a] | 168 | 403 | 2.8 | 2.8 |
| 664 | 198 | 405 | 4.1 | 3.5 |
| 664[a] | 272 | 407 | 5.8 | 3.8 |
| 663 | 349 | 402 | 7.0 | 3.6 |
| 663 | 416 | 403 | 9.8 | 4.3 |
| 663 | 596 | 1442 | 10.4 | 3.8 |
| 663 | 1055 | 1440 | 16.0 | 3.0 |

[a] Runs in packed flask six times surface.

The position of thermal equilibrium was studied by heating prepared mixtures for varying lengths of time. In Fig. 1 the percentage of original *trans* isomer is plotted against change in 500 minutes of heating time. The equilibrium constant, at 663°K., is evidently near 1.12 corresponding to 52.8% *trans* isomer. Only a few experiments were

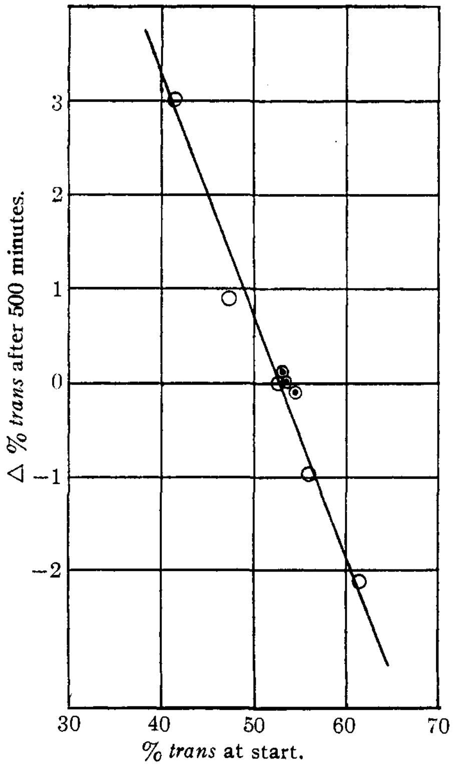

Fig. 1.—○, 663°K.; ⊙, 620°K.

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[8] Hurd and Goldsby, THIS JOURNAL, **56**, 1812 (1934).

made at a temperature of 620°K., because of the extreme slowness of the reaction, but they indicate that the position of the equilibrium is not greatly changed. This is to be expected in view of the small heat of isomerization.[5]

## Discussion of the Results

The kinetic data reported here are, on the whole, very difficult to interpret with certainty. During the course of the reaction the order appears to be somewhat less than first, but the dependence on initial pressure, below atmospheric, gives a second order reaction. This is substantially what has been observed earlier with methyl maleate.[1] The high pressure data, however, do not fit into the picture and at present lack any plausible explanation. The temperature coefficient, even allowing for a large experimental error, gives such a small activation energy (*ca.* 18,000 cal.) that the temperature independent ($A$) factor comes out to be of the order of unity. This can hardly be reconciled with the present theories of unimolecular reactions and rather than suggest, on the basis of the present results, any inconsistencies in these theories, we are inclined to attribute our results to a chain mechanism of an unknown nature. The only conclusion then which the experiments still enable one to make is that the unimolecular rate of isomerization is very slow. Even if the energy of activation is as large as was observed with stilbene (*ca.* 45,000 cal.), the $A$ factor is not larger than $10^9$. As an $A$ factor of even this magnitude is rather awkward for the present theories because there exist no reasons to suppose that a change in electronic quantum state is occurring in the reaction, the true activation energy is probably still larger.

The equilibrium composition as reported here is appreciably different from the findings of Frey and Huppke[9] but as these authors studied the equilibrium mixtures by a method which could hardly give better than approximate results and the disagreement amounts to only 8%, it is well within combined experimental errors. Using the heat of the forward reaction obtained from the heats of hydrogenation at 82°,[5] $\Delta H = -950$ cal., one finds the entropy change equal to $-1.2 \pm 0.2$ E. U., which is to be compared to Todd and Parks' value[6] of $-1.8$ E. U. at 298°K. A part of the observed entropy difference is undoubtedly of rotational origin. The products of the principal moments of inertia of the *cis* and the *trans* isomers have been calculated therefore, using Pauling's internuclear distances, tetrahedral angles and assuming that the masses of the hydrogens in the methyl groups are distributed on circles described when the methyl groups are free to rotate. The resultant rotational entropy difference is calculated to be $-0.27$ E. U. Kassel in a recent note[10] gives, using a more elaborate calculation, $-0.425$ E. U. The remainder, 0.932 or 0.77 E. U. ($\pm 0.2$), which is needed to reconcile the equilibrium constant presented here with these data, must be assigned to vibrational entropy difference. This is difficult to estimate accurately, but evidence is not lacking[11] that some frequencies at least of the *cis* isomers are lower than those of the *trans* compounds. While thus it may be possible to account for the observed entropy difference of $-1.2$ E. U. at 663°K., correcting at the same time for the change with temperature of the heat of reaction, the difference found by Todd and Parks at 298°K., $-1.8$ E. U., is not quite consistent with the rest of the experimental data. Most probably the extrapolation to absolute zero by the method of Parks[12] is not sufficiently accurate to give the small entropy differences involved in these calculations.

## Summary

1. The kinetics of the thermal *cis–trans* isomerization of butene-2 have been investigated. The reaction appears to be of approximately first order during a run but of second order with respect to initial pressure. The observed activation energy points to an $A$ factor of the order of unity and as this is most unlikely, it is suggested that the mechanism of the reaction may involve a chain.

2. The equilibrium composition of the reaction has been determined at 663°K. and at 620°K. At both temperatures, within experimental error, the composition is the same, 52.8% *trans* isomer.

MALLINCKRODT CHEMICAL LABORATORY
HARVARD UNIVERSITY
CAMBRIDGE, MASSACHUSETTS RECEIVED MARCH 6, 1936

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(9) Frey and Huppke, *Ind. Eng. Chem.*, **25**, 54 (1933).

(10) Kassel, *J. Chem. Phys.*, **4**, 144 (1935).

(11) B. Gredy, *Compt. rend.*, **196**, 938 (1933).

(12) Parks and Huffman, "Free Energies of Organic Compounds," Chemical Catalog Co., New York, 1932, p. 240.