Kinetics of the Acid-Catalyzed Isomerization of Phenylbutenes in Glacial Acetic Acid

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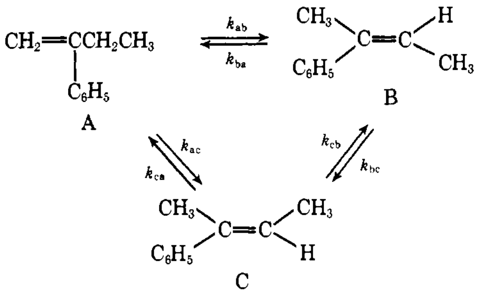
Abstract: The kinetics of the isomerization of the *cis-* and *trans*-2-phenyl-2-butenes and 2-phenyl-1-butene, catalyzed by *p*-toluenesulfonic acid in glacial acetic acid, was studied at 50°. All six rate constants for the isomerization reactions between the three isomers were determined. Unlike the results of a previous study of these reactions[1b] the results presented in this paper are in agreement with the principle of microscopic reversibility. With the assumption that the same carbonium ion was generated by proton addition to each olefin, the proportion of each olefin produced by the carbonium ion was calculated to be 65% cis, 2% trans, and 33% terminal. Under identical conditions, the carbonium ion produced by the removal of the acetate ion from 2-phenyl-2-butyl acetate gave 67% cis, 2% trans, and 31% terminal. These data imply that the conformationally different phenylbutyl carbonium ions equilibrate more rapidly than the ions lose protons.

The isomerization of the *cis-* and *trans*-2-phenyl-2-butenes and 2-phenyl-1-butene, catalyzed by *p*-toluenesulfonic acid in glacial acetic acid, was studied by Cram and Sahyun.[1b] The kinetics of the isomerization was studied by measuring the rate of disappearance of each isomer, obtaining second-order rate constants (first order in *p*-toluenesulfonic acid and first order in olefin) for the disappearance of the initial olefin. The reaction can be represented by the following quasiunimolecular reactions when the *p*-toluenesulfonic acid concentration is held constant



where A designates 2-phenyl-1-butene, B designates *trans*-2-phenyl-2-butene, and C designates *cis*-2-phenyl-2-butene. The rate constants for the disappearance of each isomer are

$$\begin{aligned} k_a &= k_{ab} + k_{ac} \\ k_b &= k_{ba} + k_{bc} \\ k_c &= k_{ca} + k_{cb} \end{aligned} \qquad (1)$$

The principle of microscopic reversibility requires that at equilibrium the rate of reaction in one direction along any path be equal to the rate in the opposite direction along that same path.[2] For the above reaction scheme, this leads to the following relations

$$\begin{aligned} k_{ab}[A]_{eq} &= k_{ba}[B]_{eq} \\ k_{bc}[B]_{eq} &= k_{cb}[C]_{eq} \\ k_{ac}[A]_{eq} &= k_{ca}[C]_{eq} \end{aligned} \qquad (2)$$

where $[...]_{eq}$ represents the equilibrium concentration. Using the six equations, 1 and 2, the six rate constants can be determined. Using the results of Cram and Sahyun,[1b] the solution of the six equations yields negative values for two of the rate constants, a physically unreal result. This indicates that either the triangular reaction scheme involving quasiunimolecular steps is incorrect or the rate data are incorrect.

The kinetics of this isomerization was reinvestigated to obtain each of the six rate constants independently of eq 2. These equations could then be used as a test of the mechanism.

Experimental Section

The three olefins were prepared as in the previous work[1b] and stored over nitrogen at 0° in the dark. The glacial acetic acid solvent was redistilled under nitrogen (bp 117–119°). Acetic anhydride (2%) was added to the solvent to ensure dryness. The concentration of *p*-toluenesulfonic acid present in the stock catalyst solutions was determined by the method used by Cram and Sahyun, titration of the solution with sodium acetate in acetic acid.

Kinetic studies were made by sealing the olefin solution (~0.2 *M*) under nitrogen in an ampoule with a rubber stopper having a self-sealing membrane through which aliquots could be removed by means of a hypodermic needle. The ampoule was placed in an oil bath at 50° regulated to ±0.01°. Aliquots removed at appropriate time intervals were added to 5 ml of water and promptly extracted with 2 ml of pentane. The pentane extracts were washed with 10% sodium hydroxide solution and then analyzed by gas chromatography. The gas chromatograph was a Loenco Model 15B with a 6-ft column packed with 4-methyl-4-nitropimelonitrile, 21.9% by weight on firebrick, maintained at 130°. Using synthetic mixtures of the olefins it was determined that the response of the detector was the same for all three isomers; thus, the fraction of total olefin present as any isomer was determined from the ratio of the peak area for that isomer to the total peak areas of the three isomers.

Results

Integration of the rate equations yields the following equations for the fractions of each isomer (where A, B, and C are the fractions of isomers A, B, and C, respectively)

$$\begin{aligned} A &= A_{eq} + A_1e^{-\lambda_1 t} + A_2e^{-\lambda_2 t} \\ B &= B_{eq} + B_1e^{-\lambda_1 t} + B_2e^{-\lambda_2 t} \\ C &= C_{eq} + C_1e^{-\lambda_1 t} + C_2e^{-\lambda_2 t} \end{aligned} \qquad (3)$$

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(1) (a) National Science Foundation Undergraduate Research Participant; (b) D. J. Cram and M. R. V. Sahyun, *J. Amer. Chem. Soc.*, **85**, 1257 (1963).

(2) *Cf.* K. J. Laidler, "Chemical Kinetics," 2nd ed, McGraw-Hill, New York, N. Y., 1965, pp 110–111.

Table I. Analyses of Reaction Mixtures. Acid-Catalyzed Olefin Isomerizations in Glacial Acetic Acid at 50.00 ± 0.01°

Time, min	Fraction of Isomer A	B	C
Olefin Starting Material: Terminal (A) (0.098 M TsOH)			
0	1.000	0	0
5	0.583	0.013	0.404
10	0.345	0.021	0.634
15	0.212	0.026	0.762
20	0.135	0.029	0.836
25	0.091	0.032	0.877
30	0.067	0.034	0.899
35	0.053	0.036	0.911
40	0.045	0.037	0.918
45	0.040	0.039	0.921
50	0.038	0.040	0.922
55	0.036	0.041	0.923
60	0.035	0.043	0.922
65	0.035	0.044	0.921
70	0.034	0.045	0.921
75	0.034	0.046	0.920
80	0.034	0.048	0.918
85	0.034	0.049	0.917
90	0.034	0.050	0.916
95	0.034	0.051	0.915
100	0.034	0.052	0.914
105	0.034	0.053	0.913
110	0.034	0.054	0.912
115	0.034	0.055	0.911
120	0.034	0.057	0.909
4420	0.030	0.159	0.811
Olefin Starting Material: Trans (B) (0.098 M TsOH)			
0	0	1.000	0
30	0.007	0.947	0.046
60	0.008	0.898	0.094
90	0.010	0.853	0.137
120	0.011	0.810	0.179
150	0.012	0.770	0.218
180	0.013	0.732	0.255
210	0.014	0.697	0.289
240	0.016	0.663	0.321
270	0.017	0.632	0.351
300	0.017	0.603	0.380
330	0.018	0.576	0.406
360	0.019	0.550	0.431
390	0.020	0.526	0.454
420	0.020	0.504	0.476
450	0.021	0.482	0.497
480	0.022	0.462	0.516
510	0.022	0.443	0.535
540	0.023	0.426	0.551
570	0.023	0.409	0.568
600	0.024	0.394	0.582
4420	0.031	0.157	0.812
Olefin Starting Material: Cis (C) (0.098 M TsOH)			
0	0	0	1.000
30	0.033	0.009	0.958
60	0.034	0.019	0.947
90	0.034	0.027	0.939
120	0.034	0.035	0.931
150	0.034	0.043	0.923
180	0.034	0.050	0.916
210	0.033	0.057	0.910
240	0.033	0.064	0.903
270	0.033	0.069	0.898
300	0.033	0.075	0.892
330	0.033	0.080	0.887
360	0.033	0.085	0.882
390	0.033	0.090	0.877
420	0.033	0.094	0.873
450	0.033	0.098	0.869
480	0.032	0.102	0.866
510	0.032	0.106	0.862
540	0.032	0.109	0.859
570	0.032	0.112	0.856
600	0.032	0.115	0.853
4420	0.030	0.158	0.812
Olefin Starting Material: Terminal (A) (0.0112 M TsOH)			
0	1.000	0	0
120	0.239	0.025	0.736
240	0.078	0.033	0.889
360	0.044	0.037	0.919
480	0.036	0.041	0.923
600	0.034	0.045	0.921
720	0.034	0.048	0.918
840	0.034	0.051	0.915
960	0.034	0.054	0.912
Olefin Starting Material: Trans (B) (0.0112 M TsOH)			
0	0	1.000	0
360	0.007	0.929	0.064
720	0.009	0.864	0.127
1080	0.011	0.805	0.184
1440	0.013	0.751	0.236
1800	0.014	0.702	0.284
2160	0.016	0.656	0.328
2520	0.017	0.615	0.368
2880	0.018	0.576	0.406
Olefin Starting Material: Cis (C) (0.0112 M TsOH)			
0	0	0	1.000
360	0.034	0.013	0.953
720	0.034	0.025	0.941
1080	0.034	0.036	0.930
1440	0.034	0.047	0.919
1800	0.033	0.056	0.911
2160	0.033	0.065	0.902
2520	0.033	0.073	0.894
2880	0.033	0.080	0.887

With A as the starting material, the coefficients are

$$\begin{aligned}
A_1 &= [\lambda_2(1 - A_{eq}) - k_a](\lambda_2 - \lambda_1)^{-1} \\
A_2 &= [-\lambda_1(1 - A_{eq}) + k_a](\lambda_2 - \lambda_1)^{-1} \\
B_1 &= [k_{ab} - \lambda_2 B_{eq}](\lambda_2 - \lambda_1)^{-1} \\
B_2 &= [-k_{ab} + \lambda_1 B_{eq}](\lambda_2 - \lambda_1)^{-1} \\
C_1 &= [k_{ac} - \lambda_2 C_{eq}](\lambda_2 - \lambda_1)^{-1} \\
C_2 &= [-k_{ac} + \lambda_1 C_{eq}](\lambda_2 - \lambda_1)^{-1}
\end{aligned} \tag{4}$$

From these equations are obtained the following relations

$$\begin{aligned}
k_a &= A_1\lambda_1 + A_2\lambda_2 \\
k_{ab} &= -(B_1\lambda_1 + B_2\lambda_2) \\
k_{ac} &= -(C_1\lambda_1 + C_2\lambda_2)
\end{aligned} \tag{5}$$

Similar expressions are obtained with B and C as the starting material.

The results of product analyses at various times are given in Table I. The procedure used to determine the rate constants was to fit the data to eq 3 and then to calculate the rate constants from eq 5.

The method for fitting the data to eq 3 was the following. Since the data were taken at equal time intervals, τ, the equation to be fitted can be rewritten

$$y_n = A_n - A_{\mathrm{eq}} = A_1 x_1^n + A_2 x_2^n \tag{6}$$

where A_n is the fraction after n time intervals; $x_1 = \exp(-\lambda_1\tau)$; $x_2 = \exp(-\lambda_2\tau)$; $t = n\tau$. Suppose x_1 and x_2 are roots of the quadratic equation: $x^2 + \rho x + \sigma = 0$. Then, $\sigma y_n + \rho y_{n+1} + y_{n+2} = 0$. Using the experimental values for the y_n's, the constants ρ and σ were determined by applying a least-squares procedure to the preceding equation. Having determined ρ and σ, the quadratic equation was solved for the two roots, x_1 and x_2, which are then used to evaluate λ_1 and λ_2. Using x_1 and x_2, a least-squares procedure was applied to eq 6 to determine A_1 and A_2.

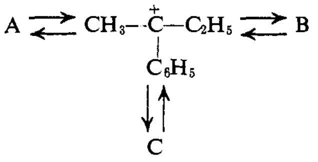
The values of the rate constants are listed in Table II. The uncertainties are expressed as the standard deviations derived from the least-squares procedures.

Unlike the previous work,[1] no significant difference was found between the second-order rate constants obtained using different concentrations of *p*-toluenesulfonic acid, 0.098 and 0.0112 *M*.

Discussion

The relationships derived from the principle of microscopic reversibility, eq 2, can be verified by comparing ratios of rate constants with ratios of equilibrium fractions: $k_{\mathrm{ab}}/k_{\mathrm{ba}} = 5.2 \pm 0.4$, $B_{\mathrm{eq}}/A_{\mathrm{eq}} = 5.26$; $k_{\mathrm{bc}}/k_{\mathrm{cb}} = 5.1 \pm 0.4$, $C_{\mathrm{eq}}/B_{\mathrm{eq}} = 5.14$; $k_{\mathrm{ac}}/k_{\mathrm{ca}} = 27 \pm 1$, $C_{\mathrm{eq}}/A_{\mathrm{eq}} = 27.1$. This good agreement shows that the data are consistent with the triangular reaction scheme presented earlier.

If the assumption is made that addition of a proton to the cis, trans, and terminal olefins produces the same carbonium ion, the mechanism can be written



$$\mathrm{A} \rightleftarrows \mathrm{CH_3{-}\underset{\displaystyle C_6H_5}{\overset{+}{C}}{-}C_2H_5} \rightleftarrows \mathrm{B}, \qquad \mathrm{C_6H_5\text{-carbonium ion}} \rightleftarrows \mathrm{C}$$

Define f_{a}, f_{b}, and f_{c} to be the fractions of terminal, trans, and cis olefins formed, respectively, by loss of a proton from the carbonium ion. These fractions are related to the rate constants by the following expressions: $f_{\mathrm{b}}/f_{\mathrm{a}} = k_{\mathrm{cb}}/k_{\mathrm{ca}}$, $f_{\mathrm{c}}/f_{\mathrm{a}} = k_{\mathrm{bc}}/k_{\mathrm{ba}}$, $f_{\mathrm{c}}/f_{\mathrm{b}} = k_{\mathrm{ac}}/k_{\mathrm{ab}}$. Using these equations and the condition: $f_{\mathrm{a}} + f_{\mathrm{b}} + f_{\mathrm{c}} = 1$, the fractions are calculated to be 0.32, 0.02, and 0.66 for f_{a}, f_{b}, and f_{c}, respectively.

Table II. Second-Order Rate Constants at 50°

	In 0.098 *M* TsOH 10^4k, M^{-1} sec^{-1}	In 0.0112 *M* TsOH 10^4k, M^{-1} sec^{-1}
k_{ab}	5.6 ± 0.2	5.5 ± 0.3
k_{ac}	180 ± 5	182 ± 8
k_{ba}	1.07 ± 0.08	1.1 ± 0.2
k_{bc}	2.15 ± 0.08	2.2 ± 0.2
k_{ca}	6.6 ± 0.2	6.7 ± 0.3
k_{cb}	0.42 ± 0.01	0.41 ± 0.02

Under the same conditions, the 2-phenyl-2-butyl cation produced by the removal of the acetate ion from 2-phenyl-2-butyl acetate gave 31% A, 2% B, and 67% C.[1] This agreement indicates that both reactions are passing through the same intermediate. This result is contrary to the conclusion reached by Cram and Sahyun; however, their calculations of the fractions were based on rate constants which were inconsistent with the principle of microscopic reversibility. In fact, a calculation of the fractions using their results and the principle gives the following values of f_{a}, f_{b}, and f_{c}: −2.18, 1.46, and 1.72, respectively. The negative value of one fraction and the values for the fractions larger than unity reflect once again the inconsistency of the data with a triangular reaction scheme involving quasi-unimolecular steps.

The main difference between the present work and the work of Cram and Sahyun is the procedure used for determining rate constants. The latter workers defined an instantaneous second-order rate constant for each experimental point. These rate constants were found to change with time due to back reaction. To correct for the back reactions, plots of the logarithms of the instantaneous rate constants as a function of time were extrapolated to zero time. However, the time interval for this extrapolation was large. Treating the data obtained in this work in this manner and extrapolating over a similar time interval gave poor results in comparison with the results obtained by fitting the integrated rate equation.

We conclude that the rate constants of the previous authors were in error and that the reaction is adequately described by a reaction mechanism with a single carbonium ion intermediate. Also, we have demonstrated the use of the principle of microscopic reversibility to test the consistency of a proposed reaction scheme with experimentally derived rate constants.

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