

tion of the original compound into a moderately stable primary product,^{3f} and this type of explanation cannot be definitely excluded at present for the case of tetrahydrofuran. In this connection it might be thought that butyraldehyde which is isomeric with tetrahydrofuran might be a possible intermediate, but the presence of butyraldehyde was not revealed in the analyses for aldehydes.

If the products of the decomposition could exhibit a sufficiently accelerating influence, as suggested by Kuchler for cyclopentane,^{3e} the shape of the pressure-time curve could be due to autocatalysis. However, definite conclusions concerning the mechanism of the decomposition of tetrahydrofuran cannot be drawn until additional experimental results are obtained.

Summary

The homogeneous decomposition of tetra-

hydrofuran has been investigated in the region 529 to 569° at pressures from 50 to 300 mm. Acetaldehyde and formaldehyde have been identified as intermediate products. The products found by gas analysis are chiefly ethylene, carbon monoxide and methane together with smaller percentages of higher unsaturated compounds, hydrogen and ethane.

The pressure measurements indicate that a slight induction period is present and that the reaction is 1.5 order. The rate constant can be expressed as

$$k = 1.15 \times 10^{12} \times e^{-53,000/RT} \text{ mole}^{-1/2} \text{ liter}^{1/2} \text{ sec.}^{-1}$$

The rate of decomposition is not retarded to any appreciable extent by either nitric oxide or propylene.

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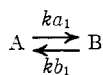
Effect of Side Reactions on Experimental Isomerization Equilibria

BY JOHN R. BATES

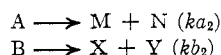
Isomerization of one hydrocarbon compound to produce another almost universally involves the use of catalyst to promote the reaction. In most cases the extent of the reaction is governed by an apparent equilibrium or stationary concentration of the two isomers. It is also true that in every instance of the use of catalyst for such purposes, side reactions other than those of pure isomerization occur. It has been generally accepted that the equilibrium reached would be governed by purely thermodynamic considerations if the same apparent equilibrium concentration were obtained when starting with each of the two isomers, irrespective of any side reactions that might occur. Kinetics of some such process are here evaluated and show that values far from calculated true equilibrium can be obtained, and confirmed by starting with either of the two isomers as the reactant.

It should be observed that these results are obviously not in contradiction with thermodynamic theory inasmuch as isomerization equilibria calculated from free energy of the isomers do not necessarily represent the lowest energy state of the system when all the possible reactions which the isomers may undergo, in addition to their transformation one to another, are considered.

Consider the reaction



with side reactions



$$B/A = \frac{2ka_1}{kb_1 + kb_2 - ka_1 - ka_2 + [(ka_1 + ka_2 - kb_1 - kb_2)^2 + 4ka_1kb_1]^{1/2}} \quad (8)$$

is the case in a number of reactions of hydrocarbons,¹ the following differential equations will hold and must be solved simultaneously.

$$-dA/dt = Aka_1 - Bkb_1 + Aka_2 \quad (1)$$

$$-dB/dt = Bkb_1 - Aka_1 + Bkb_2 \quad (2)$$

Using the well-known methods of a particular integral and auxiliary equation, the following values for A and B as a function of time are obtained.

$$ka_1A = C(kb_1 + kb_2 - \alpha - \beta)e^{-(\alpha + \beta)t} + D(kb_1 + kb_2 - \alpha + \beta)e^{-(\alpha - \beta)t} \quad (3)$$

$$B = Ce^{-(\alpha + \beta)t} + De^{-(\alpha - \beta)t} \quad (4)$$

where

$$\alpha = (ka_1 + kb_1 - ka_2 + kb_2)/2$$

$$\beta = [(ka_1 + ka_2 - kb_1 - kb_2)^2 + 4ka_1kb_1]^{1/2}/2$$

C and D can be evaluated in terms of the initial quantities of A and B as follows

$$C = \frac{-ka_1A_0 + B_0(kb_1 + kb_2 - \alpha + \beta)}{2\beta} \quad (5)$$

$$D = \frac{ka_1A_0 - B_0(kb_1 + kb_2 - \alpha - \beta)}{2\beta} \quad (6)$$

The ratio of B to A, which should yield the equilibrium K_c at $t = \infty$, is given by

$$B/A = \frac{ka_1[Ce^{-2\beta t} + D]}{C(kb_1 + kb_2 - \alpha - \beta)e^{-2\beta t} + D(kb_1 + kb_2 - \alpha + \beta)} \quad (7)$$

which at $t = \infty$ becomes

$$B/A = \frac{2ka_1}{kb_1 + kb_2 - ka_1 - ka_2 + [(ka_1 + ka_2 - kb_1 - kb_2)^2 + 4ka_1kb_1]^{1/2}} \quad (8)$$

(1) Rosen (Talicheev), *Oil Gas J.*, **39**, No. 41 (1941); also, see Burk and Laskowski, paper presented before Petroleum Division, Boston Meeting, A. C. S., 1939, for references.

If all the reactions involved are first order, which

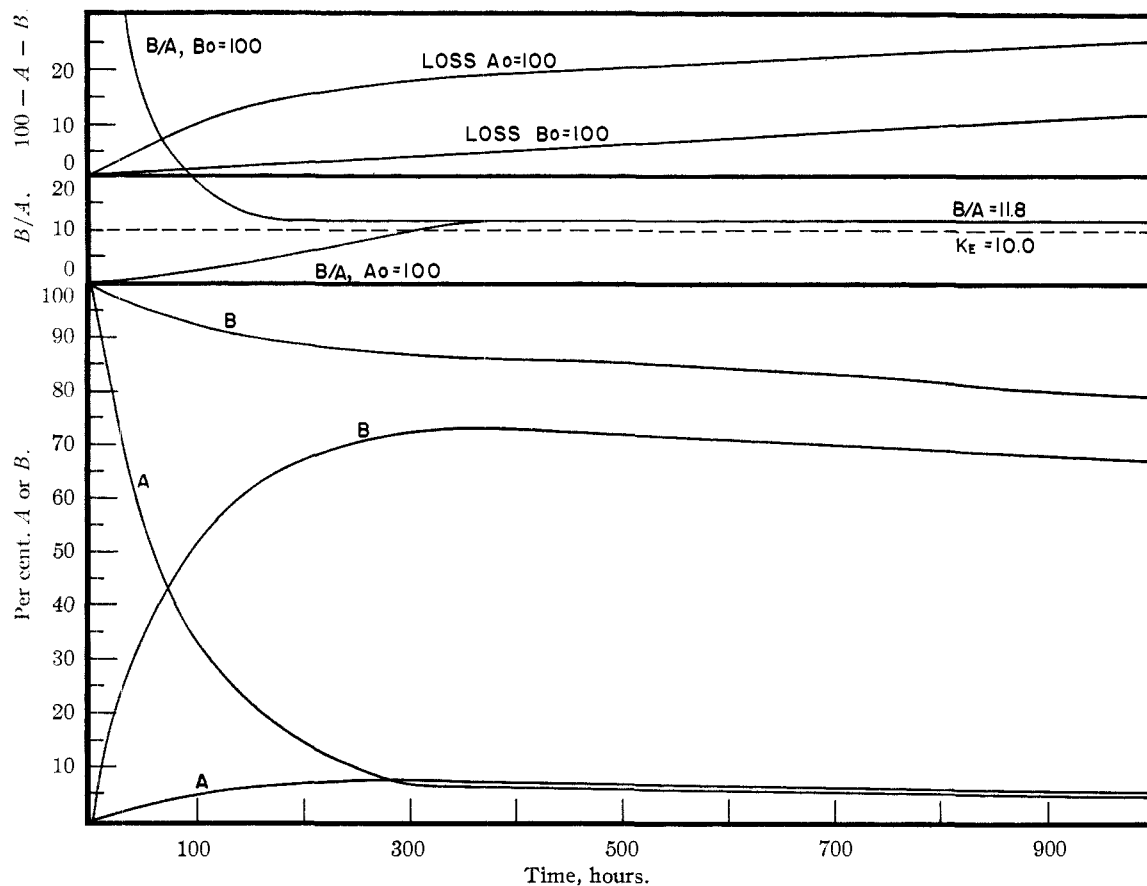


Fig. 1.—Kinetics of isomerization reaction in which $ka_1 = 0.01 T^{-1}$, $kb_1 = 0.001 T^{-1}$, $ka_2 = 0.002 T^{-1}$, $kb_2 = 0.000 T^{-1}$. In the lower section is shown variation of concentrations of A and B both when $A_0 = 100$ and when $B_0 = 100$. In the middle section, the approach to the stationary state B/A is compared with the true equilibrium ratio K_e . At the top is the total loss of $B + A$ to side reactions with time for the two cases.

Equation (8) is a definite constant value of the ratio of B/A which will be approached within errors of measurement at some time t and continue constant indefinitely with increasing time. When $ka_2 = kb_2 = 0$, $B/A = ka_1/kb_1$, the well-known value for the equilibrium constant of two opposed first order reactions, without side reactions. Equation (8) then represents a stationary state, which may be other than that indicated by free energy change and true equilibrium conditions.

The extent of the deviation of the value of B/A as given by (8), from ka_1/kb_1 will give an estimate of the magnitude of the errors to be expected in determining isomerization equilibria when side reactions occur. A number of values of B/A for varying individual reaction rate constants are shown in Table I.

The divergences between B/A and ka_1/kb_1 are from 0 to 1100% in the examples cited. It is quite evident that the difference in rates of the side reactions, ka_2 and kb_2 , is the determining factor. Example 6, which postulates that A undergoes a side reaction to the extent of 20% of the main isomerization, while B has no side

TABLE I
VALUES OF B/A AND ka_1/kb_1

No.	ka_1	ka_2	kb_1	kb_2	B/A	ka_1/kb_1	B/A ka_1/kb_1
1	1	0.01	0.1	0.01	10.0	10.0	1.00
2	1	.01	1	.01	1.0	1.0	1.00
3	1	.01	0.1	.001	10.1	10.0	1.05
4	0.01	.01	.001	.001	18.5	10.0	1.85
5	.01	.005	.001	.001	13.6	10.0	1.36
6	.01	.002	.001	.000	11.8	10.0	1.18
7	.01	.01	.005	.005	2.74	2	1.37
8	.01	.1	.001	.001	110	10	11.0
9	.01	.000	.01	.001	0.95	1.00	0.95

reaction, is one which is not at all unlikely experimentally. Example 8, in which the velocity of the side reaction of A is ten times the isomerization velocity, giving an equilibrium value eleven times that which it should, would not be often encountered in simple isomerization reactions. However, it is illustrative of what might happen in a more complicated system, such as occurs in pyrolysis or cracking of hydrocarbons. In these processes the side reaction of one compound may well predominate and produce constant concentration ratios far from those which equilibrium data demand. The amount of the compound,

which undergoes such fast side reactions, present in the resultants, would necessarily be only a small fraction of the products. In this cracking or pyrolysis type of reaction, the occurrence of small concentrations of resultants is not unusual.

To obtain a final evaluation of the results shown, it is necessary to find what loss of the isomerizing compounds is involved for a given deviation from the true equilibrium value due to side reactions. In the several cases which have been calculated in detail, it is found that the maximum percentage deviation of experimental ratio of components from equilibrium is about equal to the maximum percentage loss to side reactions as the isomerization occurs.

Obviously, when the starting point is the compound undergoing the most rapid side reactions, there will be a greater loss to by-products than when the other isomer is the starting material. The estimated possible percentage error should be based on this maximum loss. To illustrate this, the complete kinetics for example 6 is plotted in Fig. 1. The concentrations of A and B as a function of time are shown when each is the starting point. The ratio B/A and the percentage loss to by-products are also plotted. It is clearly evident that the false equilibrium is approached from both sides and that it is attained when the maximum percentage loss is about equal to the percentage deviation of the false from the true equilibrium. When starting with B, the stationary state is reached with but 2% loss to by-products.

When both compounds undergo rapid side reactions, the percentage loss may be much greater than the actual deviation from true equilibrium. There will, for example, be no deviation when the two side reactions are equal, even though a large amount of side reaction occurs (Table I, examples 1 and 2). However, when estimating the possible error in an isomerization process, this assumption of a possible error equal to the loss to by-products is safest.

A calculation of example 5 in Table I showed attainment of a false equilibrium 36% in error with losses of about 25% and 50% when starting with B and A, respectively.

Zero Order Side Reactions.—The assumption of zero order side reactions (ka_2 and kb_2) failed to yield a stationary state. The values of A and B are given by

$$A = -\frac{kb_1(ka_2 + kb_2)}{ka_1 + kb_1}t - Qe^{-(ka_1 + kb_1)t} + \frac{kb_1}{ka_1}P + \frac{kb_1kb_2 - ka_1ka_2}{(ka_1^2 + ka_1kb_1)}$$

$$B = -\frac{ka_1(ka_2 + kb_2)}{ka_1 + kb_1}t + Qe^{-(ka_1 + kb_1)t} + P$$

where

$$B_0 = P + Q$$

$$P = \frac{ka_1A_0 + ka_1B_0 + (kb_1kb_2 - ka_1ka_2)}{ka_1 + kb_1}$$

$$Q = \frac{-ka_1A_0 + kb_1B_0 - (kb_1kb_2 - ka_1ka_2)}{ka_1 + kb_1}$$

Summary

The stationary state in isomerization reactions may not represent equilibrium between isomers if side reactions occur. This is true even if the same stationary state is attained when either isomer is the reactant.

This leads to the following observations governing experimental work which has, as its purpose, the determination of the equilibria of isomerization processes:

1. The same ratio of isomers should be reached by actual experiment using either isomer as a starting point. (This is a necessary but not sufficient condition.)

2. Catalyst and conditions should be chosen to yield minimum side reactions. The error in equilibrium constant may be as great as the percentage loss of the isomers to by-products. It will not always be possible to vary the amount of side reactions, resulting in a necessary uncertainty in the measurements. Fortuitous cases will arise in which the side reactions will so occur that actual error may be less than that indicated by total by-products formed. This can be detected by a complete kinetic study.

3. The ratio of isomers at the stationary state should be preferably not too large, since the error in determination of an isomer occurring in small concentrations increases experimental error.

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