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The Kinetics of the Iodine₂-catalyzed Positional Isomerism of Butene-1. The Resonance Energy of the Allyl Radical[1]

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The rate of positional isomerization of butene-1 to butene-2, catalyzed by I_2, has been studied in the temperature range 204 to 252°. The reaction is a homogeneous, gas phase reaction with no side reactions and the butene-2 is an equilibrium mixture of cis- and trans-butenes. From the concentration dependence of the rate, it is shown that the rate law has the form

$$- \frac{d(\text{butene-1})}{dt} = K_{I_2}^{1/2} k_1 (I_2)^{1/2} [(\text{butene-1}) - \frac{1}{K_{1.2}}(\text{butene-2})]$$

where K_{I_2} is the equilibrium constant for the dissociation of I_2 and $K_{1.2}$ is the experimentally observed equilibrium constant for the isomerization. A mechanism leading to this rate law is given in eq. 9. Assuming from related reactions that $k_b = k_b'$ it is found that $\log k_a = \log (2k_1) = 9.83 \ (\pm 0.15) - 13.2 \ (\pm 0.4)/\theta$, where $\theta = (4.575T/1000)$ kcal. and k_1 is in units of liter/mole-sec. From the value of the activation energy it is shown that the allylic resonance energy in the methallyl radical (m-allyl) is about 12 ± 1 kcal.

Introduction

We have demonstrated[2] that butene-1 and butene-2 undergo a reversible, measurably slow, positional isomerization in the presence of I_2 vapor in the temperature range 200 to 300°. Since there is no other chemical reaction in the system except geometrical isomerization of the butene-2 and the mechanism had been anticipated as proceeding through an allylic H-atom abstraction by I atoms, it was felt that a detailed kinetic study would be of great value in assigning a value to the allylic resonance energy for which no reliable data exist at present.

Experimental

Materials.—C.P. grade butene-1 and -2 supplied by Matheson Company were further purified by distillations under vacuum and were stored in a flask. Analyses of samples of butenes by g.l.c. (gas-liquid chromatography) on a Perkin-Elmer type R-column (polyethylene glycol) and V-column did not give peaks for any impurities in excess of 10^{-2} mole %.

Reagent grade resublimed iodine was further purified by distillations under vacuum before use.

Procedure.—The kinetic measurements were made using a standard type vacuum line and a static method. Reactions were carried out in a Pyrex glass cylindrical vessel placed in an aluminum block furnace. Temperature of the furnace was maintained to within ±0.1° by an Electronotherm controller in conjunction with a Wheatstone bridge with a temperature-sensitive arm of platinum wire having a resistance of 90 ohms.

At first, the iodine was admitted in the vessel and its pressure was measured by means of a calibrated Bourdon spoon gage fitted with a lamp and scale arrangement. Sensitivity of the spoon gage was ±0.15 mm. Then butene was admitted. It was found as expected that the isomerization reaction was not accompanied by any pressure change. For kinetic analysis, the contents of the reaction vessel were expanded rapidly after a pre-determined time into a g.l.c. sample bulb after separating the products from iodine. This sample was run in the V-column and the amounts of butene-1, cis-butene-2 and trans-butene-2 were determined quantitatively. The accuracy of the analysis was about ±3%. The accuracy was checked by preparing mixtures of butenes of known ratio by pressure measurements and running the same sample in g.l.c. The results from pressure measurements and g.l.c. analysis agreed to within ±2%.

Data

If we consider that the positional isomerization is an I-atom catalyzed reaction in which the slow step is the attack of I atoms on the butenes, then the kinetic behavior may be represented by the opposing reactions

$$\text{I} + \text{butene-1} \underset{2}{\overset{1}{\rightleftharpoons}} \text{butene-2} + \text{I} \qquad (1)$$
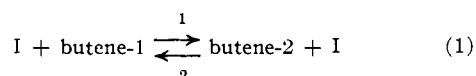
Here we neglect any kinetic differences between cis- and trans-butene-2 which we have already shown

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(2) A. N. Bose and S. W. Benson, J. Am. Chem. Soc., **85**, 1385 (1963).

to be present at all times in their equilibrium concentrations.[2] Assuming that no other slow elementary steps are involved in the process we expect for the rate law (B_1 = butene-1, B_2 = butene-2)

$$- d(B_1)/dt = k_1(B_1)(I) - k_2(B_2)(I) \qquad (2)$$

$$= k_1(I)(B_1)\left[1 - \frac{(B_2)/(B_1)}{K_{1.2}}\right] \qquad (3)$$

Here $K_{1.2} = k_1/k_2$ is the equilibrium constant for the positional isomerization and is obtained experimentally by allowing the reaction to go to equilibrium. Making use of the stoichiometry $(B_1) + (B_2) = (B_1)_0$, when butene-1 is the starting material, eq. 2 becomes

$$- d(B_1)/dt = (k_1 + k_2)(B_1)(I) - k_2(B_1)_0(I)$$

$$= \left[(B_1) - \frac{(B_1)_0}{1 + K_{1.2}}\right](k_1 + k_2)(I) \qquad (4)$$

On integration

$$\ln\left[\left(\frac{(B_1)}{(B_1)_0} - \frac{1}{1 + K_{1.2}}\right)\left(\frac{1 + K_{1.2}}{K_{1.2}}\right)\right] = -(k_1 + k_2)(I)t \qquad (5)$$

Now setting $(I) = K_{I_2}^{1/2}(I_2)^{1/2}$ where K_{I_2} is the equilibrium constant for the dissociation of I_2, we see that

$$k_{\exp} \equiv (k_1 + k_2) = k_1\left[1 + \frac{1}{K_{1.2}}\right]$$

$$= - \frac{1}{K_{I_2}^{1/2}(I_2)^{1/2}t} \times$$
$$\ln\left[\left(\frac{(B_1)}{(B_1)_0} - \frac{1}{1 + K_{1.2}}\right)\left(\frac{1 + K_{1.2}}{K_{1.2}}\right)\right] \qquad (6)$$

Hence solving for k_1

$$k_1 = - \frac{K_{1.2}/(1 + K_{1.2})}{K_{I_2}^{1/2}(I_2)^{1/2}t} \ln\left[\left(\frac{(B_1)}{(B_1)_0} - \frac{1}{1 + K_{1.2}}\right)\left(\frac{1 + K_{1.2}}{K_{1.2}}\right)\right] \qquad (7)$$

In Table I we report the values of k_1 obtained from eq. 7 at a series of different temperatures and initial concentrations. As can be seen, the form of the rate law is well obeyed over a fivefold range of I_2 pressures, a fivefold range of $(B_1)_0$ pressures and a 12 to 1 range of $(B_1)_0/(I_2)$ ratios. In the temperature range employed, $K_{1.2}$ was about 6.0. The actual values are also listed in Table I together with the appropriate values of $K_{I_2}^{1/2}$.

In Fig. 1 we show the usual Arrhenius plot of $\log k_1$ against $1/T$ from which we find the Arrhenius parameters

$$\log k_1 = 9.53 - (13.2 \pm 0.4)/\theta \qquad (8)$$

with $\theta = 4.575T$ kcal., and k_1 and A_1 expressed in units of (liter/mole-sec.). The uncertainty in $\log A$ is ±0.15.

Discussion

From our previous experience with these systems, we can write a detailed mechanism as in eq. 9.

TABLE I

KINETIC DATA FOR THE POSITIONAL ISOMERIZATION OF
BUTENE-1[a]

Temp., °K.	Time, min.	Initial concentrations $(B_1)_0$	(I_2)	Final ratio $(B_2)/(B_1)_0$	$K_{1,2}$	k_1, mm.$^{-1}$ min.$^{-1}$
477.4	260.0	44.66	7.97	0.258	6.8	5.45
	290.0	45.40	8.12	.274	(6 68)[b]	5.35
	130.0	45.80	17.98	.201		5.67
	200.0	37.20	18.00	.272		5.44
	88.0	44.38	36.98	.193		5.28
	135.0	42.70	35.97	.266		5.24
	195.0	54.20	30.13	.358		5.23
					Av.	5.38
488.5	95.0	29.69	20.64	0.270	6.4	6.55
	157.0	21.18	13.22	.320	(10.2)[b]	6.26
	85.0	19.72	36.90	.318		6.59
	105.0	36.60	29.40	.338		6.47
	120.0	29.96	27.50	.375		6.64
	95.0	41.10	25.70	.334		7.02
					Av.	6.59
497.3	40.0	49.30	25.70	0.240	6.0	9.31
	41.0	46.20	26.60	.245	(14.5)[b]	8.80
	92.0	50.40	24.50	.430		9.15
	140.0	57.10	10.88	.430		8.71
	40.0	96.40	28.80	.270		9.24
					Av.	9.04
507.8	90.0	45.50	7.54	0.450	5.7	13.4
	30.0	46.40	7.30	.180	(20.9)[b]	13.1
	25.0	48.15	32.85	.285		12.6
	30.0	29.33	31.50	.320		12.4
	32.0	62.60	28.30	.320		12.4
					Av.	12.8
525.6	15.0	21.34	22.44	0.350	5.1	16.3
	15.0	23.17	21.70	.368	(38.9)[b]	17.6
	16.0	25.34	17.00	.332		16.4
	17.0	21.72	13.40	.314		16.3
	17.0	21.00	13.50	.331		17.2
	16.0	18.10	9.78	.263		17.1
					Av.	16.8

[a] Concentrations in mm.　[b] Values of $K_{12}^{1/2} \times 10^5$ (mm.$^{1/2}$).

$$\text{butene-1} + I \underset{b}{\overset{a}{\rightleftarrows}} m\text{-allyl} + HI \underset{a'}{\overset{b'}{\rightleftarrows}} \text{butene-2} + I$$

$$+$$

$$I_2 \qquad\qquad (9)$$

$$b'' \downarrow \uparrow a''$$

$$m\text{-allyl I} + I$$

If we now assume that the concentrations of both m-allyl iodide and m-allyl radical are always small relative to butenes, which is demonstrably the case, then we can apply the "quasi-stationary" technique to these intermediates. We calculate a steady state rate law (note: $K_{1,2} = k_a k_{b'}/k_b k_{a'}$)

$$-\frac{d(B_1)}{dt} = \frac{k_a(I)(1 + 1/K_{1,2})}{(1 + k_b/k_{b'})}\left[(B_1) - \frac{(B_1)_0}{(1 + K_{1,2})}\right] \quad (10)$$

On integration this becomes

$$\frac{k_a k_{1'}}{k_{b'} + k_b} = -\frac{K_{1,2}}{1 + K_{1,2}} \frac{\ln\left[\left(\frac{(B_1)}{(B_1)_0} - \frac{1}{1 + K_{1,2}}\right)\left(\frac{1 + K_{1,2}}{K_{1,2}}\right)\right]}{K_{12}^{1/2}(I_2)^{1/2}t}$$

$$(11)$$

If we compare eq. 11 and 7 we see that our experimental value of k_1 is equal to $k_a k_{b'}/(k_{b'} + k_b) = (k_a)(k_{b'}/k_b)/(1 + k_{b'}/k_b)$. Now the ratio of $k_{b'}/k_b$

Fig. 1.—Arrhenius plot of log k_1 (units of mm.$^{-1}$ min.$^{-1}$) against $1000/T$ °K.

is just equal to the probability that the allyl radical will attack HI at the terminal or the secondary position. Our experience with radical attacks on HI is that the activation energies are of the order of 1.5 kcal./mole and about the same for all alkyl radicals. Thus we may anticipate that $k_{b'}/k_b$ will be temperature independent and very close to unity.[3] Hence we can write

$$k_a \sim 2k_1 \qquad (12)$$

In Arrhenius form (units of liter/mole-sec.)

$$\log k_a = 9.83 - 13.2/\theta \qquad (13)$$

The A factor for reaction a is about a factor of 3 lower than comparable β-H atom abstractions by I atoms from alkyl iodides and about a factor of 30 lower than H-atom abstractions by I atoms from hydrocarbons.[4] In the former cases double bond formation accompanies the abstraction as it is presumed to do in the present case so that the two appear comparable.

Now $\Delta H_{a,b} = E_a - E_b = 13.2 - E_b$. If we apply the value of $E_b = 1.5$ kcal. which has been found for reactions of CH_3 and CH_3CO with HI[5] then $\Delta H_{a,b} = 11.7$ kcal. But $\Delta H_{a,b}$ is also equal to the difference in bond dissociation energies of the C–H in butene-1 and the H–I in HI. Since the latter is 71.4 kcal.[6] we see that

$$D(\text{C–H}) = D(\text{H–I}) + 11.7 = 83.1 \text{ kcal.}$$

Let us define the allylic resonance energy as the difference in bond dissociation energies between a C–H bond conjugated with a double bond and the similar bond in a saturated paraffin. For the latter we can, in the present case, use the somewhat uncertain value of 95 kcal. as representative of secondary C–H bonds (e.g., in propane and n-butane).[5] This then yields for the allylic resonance energy the value of 12 kcal. which is very close to the value suggested by many authors.[7] The uncertainty from all causes is about ±1.0 kcal.

(3) Another argument in favor of this is that $K_{1,2} = (k_a/k_a')(k_b'/k_b)$. Now the $\Delta H_{1,2} \cong 3$ kcal. which is precisely the difference in activation energies that one anticipates for the primary and secondary H-atoms involved in k_a' and k_a, respectively. In addition, k_a' has a statistical weight of 6 to 2 for k_a in terms of active H-atoms. These two factors alone make the ratio k_a/k_a' almost equal to $K_{1,2}$.

(4) S. W. Benson, J. Chem. Phys., in press.

(5) S. W. Benson and H. E. O'Neal, ibid., 36, 2196 (1962); 37, 540 (1962).

(6) T. Cottrell, "Strength of Chemical Bonds," Butterworth, England, 1958.

(7) See P. Nangia and S. W. Benson, J. Am. Chem. Soc., 84, 3411 (1962).