

a larger group after replacement of Cl or after C–C bond break is consistent with the trend postulated on the basis of gas phase data on halocarbons,<sup>10,11</sup> even though these gas phase data have been shown in the present experiments to underestimate very seriously the primary hot yields of these products. The results themselves are therefore also consistent with the explanation that the preference for reaction with CH<sub>3</sub> arises from a lower rotational inertia of this group, thereby facilitating changes in orientation leading to successful C–T bond formation. The data on methyl

and ethyl chloride alone, however, are equally consistent with other postulates of the origin of the effects for R and Cl groups, *e.g.*, electron-withdrawing power of substituents, and furnish no method for choosing among these postulates. Further experiments with other molecules, with careful evaluation of the magnitude of primary product decomposition, are required to establish the significance of these trends.

*Acknowledgment.* The cooperation of the operating personnel of the Omaha Veterans Hospital reactor is gratefully acknowledged.

## Nitric Oxide and Iodine Catalyzed Isomerization of Olefins. IV. Thermodynamic Data from Equilibrium Studies of the Geometrical Isomerization of 1,3-Pentadiene<sup>1a</sup>

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Contribution from the Stanford Research Institute, Menlo Park, California.  
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The thermodynamics of the nitric oxide catalyzed, homogeneous, gas phase isomerization of *cis*-1,3-pentadiene  $\xrightleftharpoons[k_6]{k_5}$  *trans*-1,3-pentadiene have been studied over a temperature range between 126 and 394°. The measured values for the equilibrium constant,  $K_{5,6} = k_5/k_6$ , ranging from 3.47 to 2.23, yield a straight line when plotted as  $\log K_{5,6}$  vs.  $1/T$  (°K). The least-squares fit of our data to a quadratic equation using a regular computer regression program yields with standard error  $\Delta\bar{C}_p^{\circ}_{533} = -0.13 \pm 0.75$  gibbs/mole. Our data can be fitted to both a linear and a quadratic equation equally well yielding  $\Delta H^{\circ}_{533} = -1.04 \pm 0.03$  kcal./mole and  $\Delta S^{\circ}_{533} = -0.14 \pm 0.05$  gibbs/mole. These values deviate significantly from the comparative estimates given by Kilpatrick, *et al.*, and reported in the API tables, which necessarily have larger error limits attached to them. In contrast to our experimental values, these latter data would imply that throughout our temperature range *cis*-1,3-pentadiene is more stable than the *trans* isomer when the opposite is true. The value of  $\Delta H^{\circ}(25^{\circ}) = -1.66 \pm 0.27$  reported by Fraser, *et al.*, from heats of combustion measurements also deviates significantly from the value of  $\Delta H^{\circ}_{300} = -1.01 \pm 0.18$  kcal./mole, calculated from this work. With either NO<sub>2</sub> or I<sub>2</sub> as a catalyst, equilibrium is established much faster than with NO, which is to be expected from the differences in the reaction mechanism in the two systems. Unlike nitric oxide, NO<sub>2</sub> and I<sub>2</sub> cause large amounts of side reactions and increased difficulties in product separation.

### Introduction

The measurement of equilibrium constants of the iodine-catalyzed gas phase reactions of olefins and their

parent hydrocarbons has been shown to be a very simple, direct, and valuable method to determine precise differences in the thermodynamic properties of the reactants.<sup>2a</sup>

Applied to the *cis*–*trans* isomerization of 1,3-pentadiene, the present paper reports an appreciable amount of side reactions and considerable difficulties in product separation. This result is in contrast to the clean-cut experiments on the isomerization of 2-butene, reported earlier.<sup>2</sup>

The only important two side reactions, the polymerization of 1,3-pentadiene and the formation of diiodide in the lower temperature range, are shown to be a consequence of the considerably more stable radical intermediate formed with 1,3-pentadiene compared to 2-butene. The consecutive-step mechanism for the *cis*–*trans* isomerization discussed earlier<sup>2b</sup> involves the addition of an iodine atom to the double bond and subsequent internal rotation in the adduct radical. The addition of an I atom at the 4-position of 1,3-pentadiene generates allylic resonance in the radical intermediate. The iodine adduct radical with 1,3-pentadiene is therefore stabilized by the allylic resonance energy of 12.6 kcal.<sup>3</sup> compared to the *sec*-butyl iodide radical. Using NO as a catalyst instead of iodine, the stabilizing effect of the allylic resonance on the radical intermediate, when compared to 2-butene is just about compensated by the difference in bond strength between the secondary C· · · NO bond (37 kcal.)<sup>2b</sup> and the secondary C· · · I bond (53 kcal.)<sup>2b</sup>

The NO-catalyzed system, reported in the present paper, showed excellent reproducibility and no measurable side reactions. NO<sub>2</sub> gave rise to the same

(1) (a) This work has been supported in part by Grant PAU-5235 from the Public Health Service to Stanford Research Institute; (b) Postdoctorate Research Fellow.

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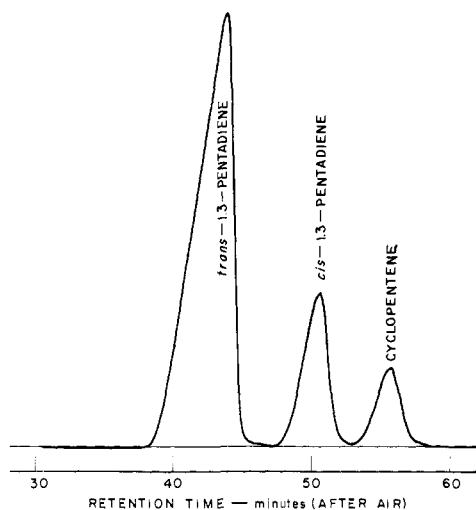


Figure 1. Chromatogram of crude piperylene (after removal of the volatile impurity fraction).

difficulties discussed for the iodine catalysis. This is to be expected from the C-ONO bond strength of about 54 kcal.

This paper reports measurements of the equilibrium constant for the geometrical isomerization of 1,3-pentadiene. A subsequent paper<sup>4</sup> will discuss the kinetics of the same system.

### Experimental

*A. Procedure and Apparatus.* Method and experimental set-up used in these experiments have been reported in detail earlier.<sup>2a</sup> The study consisted of mixing NO and hydrocarbon in the vapor phase in a static system and analyzing the reaction products following the quenching of the reaction.

The reaction vessels used have either been coated with Teflon or silicone oil (Dow Corning 705) and showed no measurable wall effects.<sup>4</sup>

*B. Materials.* 1,3-Pentadiene (*cis* and *trans*) was prepared from 92% piperylene (7% cyclopentene) obtained from the Aldrich Chemical Co. (Milwaukee, Wis.). Separation of the isomers was achieved by careful fractional distillation and selectivity in forming chemical adducts. *trans*-1,3-Pentadiene adds (1,4) fast and at room temperature irreversibly to maleic anhydride<sup>5-7</sup> while the *cis* isomer does not react. *cis*-1,3-Pentadiene forms a reversible complex with CuCl,<sup>5,6</sup> while the *trans* isomer is not affected under the same conditions. The purity of the 1,3-pentadienes used in this study was 99.65% (0.3% *cis*, 0.05% cyclopentene) for *trans* and for *cis* 99.75% (0.25% *trans*).

Lecture bottle NO obtained from Matheson Chemical Co. (East Rutherford, N. J.) was purified by passing it through silica gel, Ascarite, and KOH and resubliming the NO(s) several times.<sup>8</sup>

*C. Analysis.* Analysis of the product was carried out by gas-liquid chromatography, with a Model 720 F & M gas chromatograph, using a 20-ft. 0.25-in.

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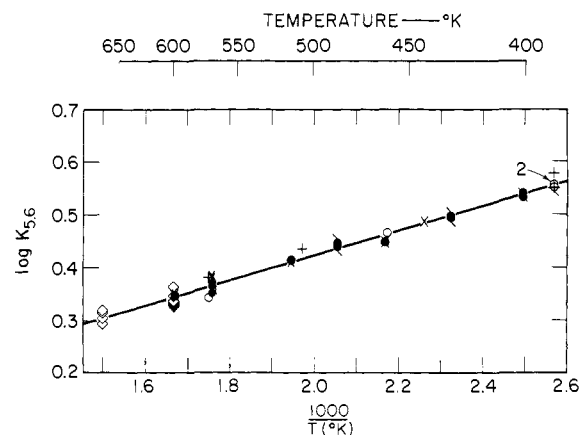


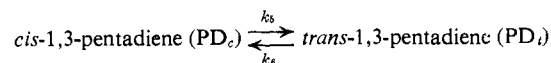
Figure 2. Arrhenius plot of the equilibrium constant for the geometrical isomerization of 1,3-pentadiene. Equilibrium values obtained with NO as a catalyst are indicated with  $\times$  starting with the *trans* isomer,  $\bullet$  starting with the *cis* isomer.  $\bullet$  is used for a starting isomer mixture rich in *trans*,  $\circ$  for a mixture rich in *cis*. Results with I<sub>2</sub> as a catalyst are represented similarly with +,  $\circ$ ,  $\diamond$ , and  $\square$ . Results from kinetic studies are incorporated  $\diamond$ .

column filled with firebrick mesh size 60-80, with a 20% coating of Dow Corning silicone oil 710. The quantitative separation of the *cis* and *trans* isomers and cyclopentene was better than 99%. The measured ratios of the isomers were generally reproducible to within  $\pm 1\%$  (maximum deviation). The column was operated at 10° with a He flow rate of 120 ml./min., and the following retention times in minutes (after air) have been measured: *trans*-1,3-pentadiene, 43.7; *cis*-1,3-pentadiene, 51.7; cyclopentene, 57.0. Results with other column materials reported in the literature showed less satisfactory results.<sup>9-13</sup>

A typical chromatogram is shown in Figure 1.

### Results

By analogy with the isomerization of 2-butene,<sup>2a</sup> the equilibrium constant for the process



is given by

$$K_{5,6} = \frac{k_s}{k_e} = \frac{(\text{PD}_t)}{(\text{PD}_c)}$$

The results of measurements of  $K_{5,6}$  using iodine and NO as catalysts are listed in Table I. Also listed are additional data obtained incidently during kinetic studies on the positional isomerization of 1,4-pentadiene to 1,3-pentadiene and from measurements of the dimerization of 1,3-pentadienes.

Figure 2 shows a plot of  $\log K_{5,6}$  vs.  $1/T$  for the same data. Only part of the data, obtained with iodine as a catalyst are incorporated in Table I and Figure 2, and they are not used to compute the Arrhenius parameters. The results with iodine merely show that equilibrium is established with both catalysts, NO and iodine. With iodine, equilibrium is reached more than 1000 times

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**Table I.** Composition of Equilibrated Mixtures of *cis*- and *trans*-1,3-Pentadiene

Temp., °K.	Catalyst press., mm.		Starting compd. Iso- mer <sup>a</sup>	Press., mm.	Time, min.	Final equil. ratio <i>t/c</i> = <i>K</i> <sub>5,6</sub>	Log <i>K</i> <sub>5,6</sub>
	I <sub>2</sub>	NO					
399.1		115.5	4.2	41.9	3909	3.41	0.5328
401.0		216.9	2.8	44.9	4013	3.47	0.5408
430.6		60.3	4.2	54.0	105	3.85	0.5849 <sup>b</sup>
		70.5	1.94	46.8	214	2.32	0.3646 <sup>b</sup>
		151.5	4.2	44.7	940	3.13	0.4953
		126.0	2.8	39.2	369	3.14	0.4962
442.5		60.8	<i>t</i>	50.1	1013	3.07	0.4876
		44.4	<i>c</i>	32.3	912	2.27	0.3556 <sup>b</sup>
461.2		108.8	<i>t</i>	74.5	796	2.80	0.4475
		61.5	<i>c</i>	56.4	961	2.80	0.4476
486.9		76.5	<i>t</i>	65.7	98	2.96	0.4713 <sup>b</sup>
		45.3	3.20	42.3	63	2.79	0.4456
		56.2	<i>c</i>	34.4	73	1.43	0.1553 <sup>b</sup>
		72.8	<i>c</i>	43.0	141	2.33	0.3674 <sup>b</sup>
		125.0	1.79	39.7	126	2.75	0.4398
513.7		119.6	<i>t</i>	45.2	220	2.56	0.4086
		69.6	<i>c</i>	49.9	210	2.59	0.4128
568.5		33.2	<i>c</i>	22.4	84	1.95	0.2909 <sup>b</sup>
		47.2	<i>t</i>	52.6	66	2.42	0.3838
		90.5	<i>t</i>	37.7	95	2.40	0.3809
		36.0	1.79	51.0	63	2.37	0.3748
		98.2	<i>c</i>	23.6	63	2.25	0.3522
		84.2	1.10	29.7	31	2.32	0.3659
598.8		74.9	<i>c</i>	45.8	30	2.23	0.3475
		25.4	<i>t</i>	25.4	78	2.23	0.3483
389.7	5.9		<i>t</i>	36.9	20	3.57	0.5527
	3.3		<i>t</i>	61.5	17	3.79	0.5786
	0.5		<i>t</i>	52.0	28	4.47	0.6503 <sup>b</sup>
	0.6		<i>c</i>	17.0	16	1.68	0.2253 <sup>b</sup>
	1.5	3.20		67.7	60	3.59	0.5551
	2.2	3.20		68.0	108	3.59	0.5551
	2.3	3.78		74.9	63	3.55	0.5502
460.4	2.5		<i>c</i>	15.6	9.5	2.92	0.4654
507.3	1.5		<i>t</i>	267	7.	2.72	0.4357
571.8	0.1		<i>t</i>	10.5	1.5	2.40	0.3809
	0.1		<i>c</i>	6.4	1.5	2.20	0.3424
602.7		61.6	1,4-PD	89.9	180	2.16	0.3345
		21.9	1,4-PD	54.2	920	2.23	0.3483
		180.0	1,4-PD	180.0	324	2.18	0.3385
			4.2	85.1	4320	2.13	0.3284 <sup>c</sup>
			4.2	120	4319	2.31	0.3636 <sup>c</sup>
667.3		275	1,4-PD	144	16	1.97	0.2951
		102.3	1,4-PD	127.5	26	2.06	0.3139
		107.5	1,4-PD	63.0	90	2.09	0.3201
		143.9	1,4-PD	66.9	250	2.02	0.3060

<sup>a</sup> *t* and *c* stand for *trans*- and *cis*-1,3-pentadiene and 1,4-PD for 1,4-pentadiene. Where a number is given, it corresponds to the initial isomer mixture [*t/c*]<sub>0</sub>. <sup>b</sup> Did not reach equilibrium, the product of catalyst pressure and time being too small. <sup>c</sup> Results from studies on the thermal dimerization of 1,3-pentadienes.

faster than with NO, but the data show an unusually large scatter which was found to be related to side reactions involving 1,3-pentadiene, such as polymerization and, in the lower temperature range around 400°K., the formation of diiodides. In addition, the separation of the hydrocarbons from the iodine while quenching the reaction was not always quantitative, owing to the hydrodynamic sweeping of iodine vapor along with the hydrocarbons. The effect was especially large with pressure ratios of iodine to pentadiene  $\geq 0.2$ . Secondary reactions in the condensed phase could therefore have contributed to the scatter in the equilibrium values by altering the ratio of the products. In contrast to the iodine catalysis, equilibrium data obtained with NO showed excellent reproducibility independent

of initial composition and pressure. The least-squares fit of our data using a regular regression program on a B 550 computer yields with standard errors

$$2.303R \log K_{5,6} = -(0.14 \pm 0.05) + \frac{(1037 \pm 28)}{T}$$

with *R* in cal./mole °K.

### Discussion

There are only a few semiquantitative values for *K*<sub>5,6</sub> available from literature data.<sup>5,14</sup> Frank, *et al.*,<sup>5</sup> measured the composition of an equilibrated isomer mixture after refluxing either *cis*- or *trans*-1,3-pentadiene with traces of iodine. Their results lead to a value for PD<sub>*t*</sub>/PD<sub>*c*</sub> of 6.1 ± 0.5. Assuming a temperature of ~42° we would predict *K*<sub>5,6</sub> to be 5.0 instead. The same authors measured the composition of the isomer mixture obtained after passing either *cis*- or *trans*-1,3-pentadiene through a vertical tube at 600°. PD<sub>*t*</sub> yielded a *trans* to *cis* ratio of 1.2; starting with PD<sub>*c*</sub> the ratio was 1.5, compared to the expected value of 1.66 from this work. Rohrer and Sinfelt<sup>14</sup> used alumina as a catalyst in a microreactor study, and from their results one can calculate a value for *K*<sub>5,6</sub> of 1.71 at 527°, in good agreement with our extrapolated value of 1.75. In view of the rather crude measurements, all these data are consistent with the results of this work.

Only very few calorimetric measurements on 1,3-pentadienes have been reported in the literature. Dolliver, *et al.*,<sup>15</sup> reported the heat of hydrogenation of a mixture of the isomers as 54.1 ± 0.15 kcal./mole at 355°K. Fraser and Prosen<sup>16</sup> measured the heat of combustion for *cis*- and *trans*-1,3-pentadiene, yielding a value of Δ*H*°(25°) = -1.66 ± 0.27 kcal./mole for the standard heat of isomerization. This value is in line with our results but does not agree within the error limits quoted by the authors (using a value for Δ*C*<sub>p</sub>° = -0.13 ± 0.75, resulting from this work). Kilpatrick, *et al.*,<sup>17</sup> evaluated the thermodynamic functions for *cis*- and *trans*-1,3-pentadiene, by combining the thermodynamic functions for other compounds, for which values had already been calculated. From the combination of the heat of hydrogenation<sup>15</sup> and the heat of formation of pentane,<sup>18</sup> the authors calculate values for the heat of formation of *cis*- and *trans*-1,3-pentadiene for the temperature range from 300 to 1500°K. These values have necessarily large error limits attached, and the authors estimate the uncertainty in the heat of formation to be ±0.75 kcal./mole, which makes the value for the heat of isomerization calculated from these data tenuous.

The direct experimental data presented in this paper lead to reliable values for Δ*H*°<sub>T</sub>, Δ*G*°<sub>T</sub>, and Δ*S*°<sub>T</sub> for the isomerization of 1,3-pentadiene in the temperature range between 400 and 670°K. Our data have been fitted to both a linear and a quadratic equation using a standard least-squares fit regression program on an IBM B 550 computer. As a measure of the

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accuracy of the fit one can look at the multiple correlation coefficient, which would equal 1.000000 in the case of a perfect fit. The fit of our data to a linear equation yields a value of 0.990663 for the multiple correlation coefficient, compared to 0.990675, using the quadratic equation. This then means, that our data can be fitted to both a linear and a quadratic equation equally well. The fit to the quadratic equation yields, with standard errors

$$\log K_{5,6} = -(4042 \pm 23414)/T^2 + (242.5 \pm 92.6)/T - (0.046 \pm 0.0089)$$

and from the coefficient of the  $(T)^{-2}$  term one obtains a value for the mean  $\overline{\Delta C_p^\circ}$  at 533°K.

$$\overline{\Delta C_p^\circ}_{533} = -0.13 \pm 0.75 \text{ gibbs/mole}$$

From both the coefficients of the linear as well as the quadratic equation, one calculates (with standard errors)

$$\Delta H^\circ_{533} = -1.04 \pm 0.03 \text{ kcal./mole}$$

$$\Delta S^\circ_{533} = -0.14 \pm 0.05 \text{ gibbs/mole}$$

Using our value of  $\overline{\Delta C_p^\circ}_{533} = -0.13 \pm 0.75$  gibbs/mole and neglecting any small temperature dependence of  $\Delta C_p^\circ_T$  in the temperature range between 300 and 670°K., we calculate (with standard errors)

	300°K.	400°K.	670°K.
$\Delta H^\circ_T$ (kcal./mole)	$-1.01 \pm 0.18$	$-1.02 \pm 0.11$	$-1.06 \pm 0.11$
$\Delta S^\circ_T$ (gibbs/mole)	$-0.07 \pm 0.43$	$-0.10 \pm 0.22$	$-0.17 \pm 0.17$

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## Iodine and Nitric Oxide Catalyzed Isomerization of Olefins. V. Kinetics of the Geometrical Isomerization of 1,3-Pentadiene, a Check on the Rate of Rotation about Single Bonds, and the Allylic Resonance Energy<sup>1a</sup>

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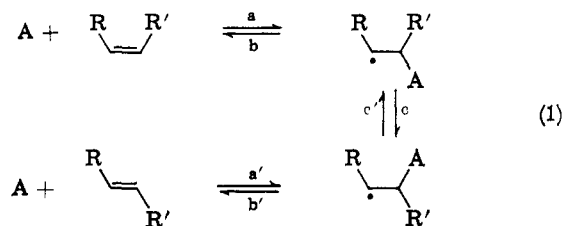
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The kinetics of the nitric oxide catalyzed, homogeneous, gas phase isomerization of *cis*-1,3-pentadiene ( $PD_c$ )  $\rightleftharpoons$  *trans*-1,3-pentadiene ( $PD_t$ ) have been studied over a temperature range between 126 and 326°. The rate law for the NO-catalyzed isomerization has the form  $-dPD_c/dt = k_5(PD_c)(NO)[1 - (PD_t)/K_{5,6}(PD_c)]$ . The equilibrium constant  $K_{5,6} = k_5/k_6$  was measured independently. The observed rate constant  $k_5$  (l./mole sec.) can be represented by  $\log k_5 = 7.26 \pm 0.3 - 18.15 \pm 0.70/\theta$ , where  $\theta = 2.303RT$  in kcal./mole. As has previously been shown the consecutive-step reaction mechanism involves NO addition to the double bond and subsequent rotation about the C-C bond in the intermediate radical:  $NO + PD_c \xrightleftharpoons[b]{a} PD_c \cdot NO \xrightleftharpoons[c']{c} PD_t \cdot NO \xrightleftharpoons[a']{b'} PD_t + NO$ . Analysis of the data shows that the rate-controlling step in the NO-catalyzed geometrical isomerization of pentadiene is the rotation about the single bond in the intermediate radical. Iodine is shown to form a much more stable intermediate radical, and results indicate that, in the  $I_2$ -catalyzed system, the addition reaction of I atoms is rate controlling. Using our observed rate constant  $k_5$  and estimates of  $K_{a,b}$ , which have been tested in an earlier paper, we can calculate the rotational rate constant  $\log k_c$  to be  $(11.5$

$\pm 0.3) - (5.3 \pm 1.0)/\theta \text{ sec.}^{-1}$  compared to  $(11.2 - (3.8)/\theta \text{ sec.}^{-1}$  as reported earlier for the iodine catalyzed *cis-trans* isomerization of 2-butene.  $K_{a,b}$  is estimated, using the previously measured value of  $12.6 \pm 1 \text{ kcal./mole}$  for the allylic resonance energy and an estimate of 37 kcal. for the C-N bond dissociation energy in alkylnitroso compounds. Both these values appear to be correct to within the reported  $\pm 1 \text{ kcal.}$

### Introduction

The iodine-catalyzed, homogeneous, gas phase *cis-trans* isomerization of 2-butene has been reported earlier.<sup>2</sup> From these results and a large number of known, related studies on catalyzed and thermal *cis-trans* isomerizations reported by other authors, it has been shown that all of these data are consistent with a consecutive-step mechanism, involving the formation of an intermediate radical and subsequent internal rotation in this radical. Letting A denote a radical catalyst



(1) (a) This work has been supported in part by Grant PAU 5235 from the Public Health Service to Stanford Research Institute; (b) Postdoctorate Fellow.

(2) S. W. Benson, K. W. Egger, and D. M. Golden, *J. Am. Chem. Soc.*, **87**, 468 (1965).