

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.
$\Delta H^\circ_T(\text{kcal./mole})$	-1.01 ± 0.18	-1.02 ± 0.11	-1.06 ± 0.11
$\Delta S^\circ_T(\text{gibbs/mole})$	-0.07 ± 0.43	-0.10 ± 0.22	-0.17 ± 0.17

(18) E. J. Prosen and F. D. Rossini, *J. Res. Natl. Bur. Std.*, **34**, 255 (1945).

(19) "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," American Petroleum Institute, Carnegie Press, Pittsburgh, Pa., 1953.

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^{1a}

Kurt W. Egger^{1b} and Sidney W. Benson

Contribution from the Stanford Research Institute, Menlo Park, California.

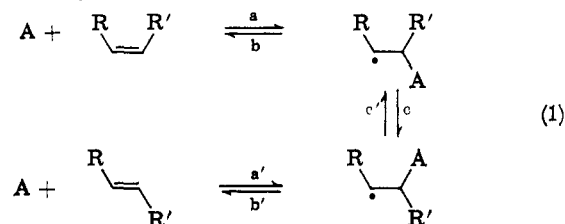
Received January 16, 1965

The kinetics of the nitric oxide catalyzed, homogeneous, gas phase isomerization of *cis*-1,3-pentadiene (PD_c) $\xrightleftharpoons[k_6]{k_5}$ *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: $NO + PD_c \xrightleftharpoons[b]{a} PD_c \cdot NO \xrightleftharpoons[c']{c} PD_t \cdot NO \xrightleftharpoons[a']{a} PD_t + NO$. 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 alkyl nitroso 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.² 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).

This scheme leads to the conclusion, that for all these *cis-trans* isomerizations either the radical formation or the internal rotation in this radical is the rate-controlling step.

In the case of the iodine-catalyzed geometrical isomerization of 2-butene, the rate is rotation controlled, and the rotational rate constant k_c was found to be equal to $10^{11.2} 10^{-3.8/\theta}$ (sec.^{-1}) which compares well with the value of $10^{11.3} 10^{-3.5/\theta}$ (sec.^{-1}) estimated from transition-state theory. ($\theta = 2.303RT$ in kcal./mole.)

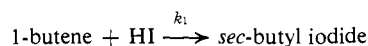
For any atom- or radical-catalyzed *cis-trans* isomerization, the reported mechanism leads to a rotation-controlled rate if the bond strength of the secondary C-A bond and any resonance energy introduced by R or R' do not add up to the value for the π -bond which is being broken (*i.e.*, if $\Delta H^\circ_{a,b}$ is positive). It was therefore of interest to check the proposed reaction mechanism and earlier results reported for 2-butene² using a diolefin molecule that generates an allylic resonance energy (12.6 kcal.³) in the radical intermediate. Owing to the differences in strength of the secondary C-A bond [53 kcal.⁴ with I or 37 kcal.² with NO as a catalyst (A)], the measured isomerization rate should be addition controlled in the case of iodine and rotation controlled using nitric oxide as catalyst. Kinetic studies on the I- and NO-catalyzed *cis-trans* isomerization of 1,3-pentadiene are reported in this paper, and the results verify the above predictions.

Experimental

A. Procedure and Apparatus. The method and experimental set-up used in these experiments have been reported on in detail earlier.⁵ 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 after a measured time.

B. Surface Effects. Isomerization and polymerization reactions of 1,3-pentadiene proved to be extremely sensitive to surface catalysis. It was therefore imperative to eliminate any possibility of reactions at the walls. The absence of any surface effects on the isomerization rate was tested two ways. (1) The kinetic measurements were carried out in two equivalent Pyrex glass vessels, one of which was packed with glass tubing. The packed vessel had an 18-fold larger surface-to-volume ratio than the unpacked one.

In order to check the surface activity of the reaction system without going through the tedious job of changing the reaction vessels too often, we used surface-sensitive addition of HI to 1-butene as a test reaction. The homogeneous rate constant for the reaction



has been estimated by Nangia and Benson⁶ from the analogous reaction with propylene and 2-butene to be $\log k_1 = 7.56 - 23.5/\theta$ (l./mole sec.). This means that at a temperature of 430°K. with ~ 50 torr pres-

sure the half-life of the reaction is of the order of 10^8 sec. The test system should therefore be completely stable at these temperatures unless the reaction takes place on the walls of the vessel.

Conditioning of the reaction vessels by performing a series of reactions of either the HI addition to 1-butene or the polymerization of 1,3-pentadiene only decreased the surface activity but did not stop the surface catalysis. Reproducible, homogeneous, gas phase reactions were only obtained in vessels that had been coated with either Teflon or Dow Corning 705 silicone oil. These coatings were obtained as follows. Teflon was decomposed at 470°, yielding more than 90% monomer, which was collected over liquid nitrogen.

About 1 vol. % di-*t*-butyl peroxide is added in the gas phase and the mixture expanded into the reaction vessel to yield a pressure between 200 and 500 torr. The vessel was kept at 605°K., and the reaction started immediately. The resulting Teflon "coating" consisted of an opaque, nonuniform layer with occasional growth of "popcorn polymers," depending on the reaction time used, which varied between one and several hours.

The silicone oil coating was applied to the vessel while disconnected from the reaction system. A 1:1 mixture of Dow Corning silicone oil 705 and CCl_4 was used to coat the surface, which was subsequently cleaned several times with pure CCl_4 solvent. This procedure resulted in a very thin coating of silicone oil. The vessel was then heated to 550°K. and cured for several hours under vacuum.

In vessels coated as described, 1,3-pentadiene shows no pressure change over several hours at a temperature of 500°K. This is in agreement with the reported⁷ homogeneous polymerization rates (k_p); $\log k_p$ at 500°K. = $-6.5 \text{ mm.}^{-1} \text{ min.}^{-1}$. With NO as the catalyst the *cis-trans* isomerization was the only measurable reaction in the system. Using iodine as a catalyst resulted in a much larger scatter of the data owing to a considerable amount of side reactions. The most important of these side reactions are the polymerization and the formation of diiodides at the lower temperatures. The difference in the behavior of the system using NO or I_2 as catalysts is attributed to the increased stability of the adduct radical in the case of iodine.

C. Materials. Preparations and purification of the materials used was reported earlier.^{5b} The purity of *trans*-1,3-pentadiene was 99.65% (0.3% *cis* and 0.05% cyclopentene), of *cis*-1,3-pentadiene 99.75% (0.25% *trans*). The purity of the NO could be estimated from the color of the liquid. Pure NO forms a white condensate and is colorless in liquid phase. Increasing traces of higher oxides give the liquid first a slightly blue, then a green tint. There was no measurable effect on the isomerization rate using NO of "clear blue or green" shadings as the amount of the impurities is extremely small. If the amount of higher oxides in NO is of the order of 1%, there is a very large effect in the isomerization rates (compare Table I, run of footnote f). It was therefore important to keep oxygen out of the system. After coating and conditioning, the vessel was therefore never exposed to air and was

(7) J. B. Harkness, G. B. Kistiakowsky, and W. H. Mears, *ibid.*, 5, 682 (1937).

(3) K. W. Egger, D. M. Golden, and S. W. Benson, *J. Am. Chem. Soc.*, 86, 5420 (1964).

(4) P. S. Nangia and S. W. Benson, *ibid.*, 86, 2773 (1964).

(5) (a) D. M. Golden, K. W. Egger, and S. W. Benson, *ibid.*, 86, 5416 (1964); (b) K. W. Egger and S. W. Benson, *ibid.*, 87, 3311 (1965).

(6) P. S. Nangia and S. W. Benson, *J. Chem. Phys.*, 41, 530 (1964).

Table I. Kinetic Data for the *cis-trans* Isomerization of 1,3-Pentadiene

Temp., °K., and vessel ^a	NO ^b press., torr	1,3-Pentadiene		Time, min.	$K_{5,6}$	PD _t /PD _c ^c	$k_5 \times 10^5$, mm. ⁻¹ min. ⁻¹	Press. change, torr ^d		
		Isomer ^e	Press., torr							
400.0	49.2	<i>c</i>	70.9	135	3.47	0.047	0.722	0.5		
	47.0	<i>t</i>	116.2	240		49.8	0.556	0.8		
	183.9	<i>t</i>	40.9	61		53.4	0.627	0.7		
	79.9	<i>c</i>	37.8	71		0.032	0.580	0.3		
	45.8	<i>c</i>	93.5	187		0.048	0.572	0.4		
	74.4	<i>t</i>	43.6	390		31.0	0.402	0.6		
430.1 p	73.1 g	<i>t</i>	28.6	27	3.14	31.5	5.19	0		
	46.5 g	<i>t</i>	107.8	91		18.4	4.32	0		
461.2 p	34.5	<i>c</i>	40.0	29	2.89	0.124	11.97	0		
	29.7 g	<i>c</i>	57.8	44		0.122	9.00	0.1		
	30.0 b	<i>c</i>	58.4	44		0.119	8.80	0.2		
	29.9 b	<i>c</i>	58.3	44		0.143	10.68	0.2		
	29.7 u	<i>c</i>	59.1	44		0.180	13.24	0.4		
	29.8 u	<i>c</i>	65.0	44		0.181	13.27	0.4		
	30.7	<i>c</i>	57.2	44		0.120	8.76 ^e	...		
	30.2	<i>c</i>	61.0	44		0.263	18.50 ^f	...		
	513.7	24.6 b	<i>t</i>	84.0		8	2.56	23.7	57.80	0.6
		21.7 b	<i>t</i>	134.9		28		10.2	46.20	0.4
		64.5 b	<i>c</i>	103.5		6		0.181	45.05	0.3
		13.5 b	<i>c</i>	58.6		28		0.309	76.15	0.3
57.3 b		<i>c</i>	93.2	6	0.170	47.60		0.3		
598.8	5.1 b	<i>c</i>	48.5	11	2.23	0.432	700.8	...		
	16.7 b	<i>c</i>	43.0	8		1.028	627.0	0.3		
	16.3 b	<i>c</i>	70.4	5		0.637	701.5	0.4		
	5.7	<i>c</i>	39.3	5		0.281	909.0	0.2		
	6.3	<i>t</i>	49.6	5		9.55	814.0	0.3		
	12.2	<i>t</i>	51.4	5		7.090	579.0	...		

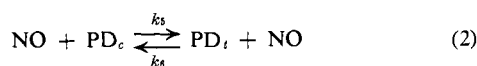
^a p = packed vessel. ^b g and b indicate NO with a green (g) or blue (b) tint, and u stands for NO which was already used in an earlier run. NO g, b, or u have different grades of traces of impurities. ^c *t* and *c*, PD_t and PD_c, stand for 1,3-pentadiene, *trans* and *cis*, respectively. ^d Total pressure loss. ^e 2.8 torr H₂O vapor added to the reaction vessel before the run was started. ^f 2.9 torr air = 0.6 torr O₂ added to the reaction vessel together with NO.

always kept under vacuum or under nitrogen (high-purity) pressure.

D. Analysis. Analysis of the product was carried out by gas-liquid chromatography, reported in detail earlier.⁵ The quantitative separation of the *cis* and *trans* isomers and cyclopentene was better than 99%. The measured PD_t/PD_c ratios were generally reproducible to within ±1% (maximum deviation), and the difference between three measurements never exceeded 5% even at total conversions as low as 3% of the initial isomer concentration.

Results

For the NO-catalyzed reaction



the rate expression for the disappearance of *cis*-1,3-pentadiene with time is

$$-\frac{d(\text{PD}_c)}{dt} = k_5(\text{PD}_c)(\text{NO}) \left[1 - \frac{(\text{PD}_t)}{K_{5,6}(\text{PD}_c)} \right] \quad (3)$$

This yields upon integration

$$k_5 = -\frac{K_{5,6}(K_{5,6} + 1)}{(\text{NO})t} \times \ln \left[\left(\frac{(\text{PD}_c)}{(\text{PD}_c^0)} - \frac{1}{1 + K_{5,6}} \right) \left(\frac{K_{5,6} + 1}{K_{5,6}} \right) \right] \quad (4)$$

where $K_{5,6} = k_5/k_6$ is the equilibrium constant of reaction 2, reported earlier,^{5b} and $(\text{PD}_c)/(\text{PD}_c^0) = 1/[1 + (\text{PD}_t)/(\text{PD}_c)]$ is the ratio of *cis*-1,3-pentadiene in the product to the initial amount of the *cis* isomer.

For the experiments, where PD_t was used, k_6 is calculated correspondingly, and k_5 is obtained from the equilibrium constant.



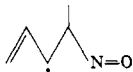
Table I contains values for the rate constant k_5 obtained from eq. 3. The values of k_5 , reported in Table I, scatter by as much as ±25% at a given temperature. The expected error in k_5 from all sources is however only ±12%. This unexpectedly large scatter of the data seems to be random and independent of experimental parameters.

The isomerization, as well as the dimerization, of 1,3-pentadienes is extremely surface sensitive. Great care was taken to eliminate any heterogeneous reactions. (See experimental section.) For an 18-fold change in surface-to-volume ratio between the unpacked and packed vessel, the measured rate constant k_5 increases by a factor of 1.8. This is considered a small change, but nevertheless it shows that there is some surface effect that we were unable to eliminate.

Small amounts of oxygen enhance the reaction through the formation of NO₂ (run of footnote *f*, Table I). Oxygen was very carefully kept out of system and materials used, as discussed earlier in the experimental section.

Small amounts of water vapor seem to have no effect on the isomerization rate (run of footnote *e*, Table I). In this system, the dimerization is the most likely side reaction and could lead to the measured pressure loss, shown in the last column of Table I. (A study of the dimerization of 1,3-pentadiene is in progress.) The radical intermediates (primary and secondary) add to 1,3-pentadiene to form cyclohexene derivatives. Assuming that this dimerization reaction

Table II. Thermodynamic Data for Calculation of $K_{a,b}$

Species	S° , gibbs/mole		C_p° , gibbs/mole	
	300°K.	500°K.	300°K.	500°K.
NO		54.1 ^a	7.1 ^a	7.3 ^a
	77.0 ^{a,b} (76.0) ^c	92.3 ^b (91.7) ^c	22.7 ^a	35.3 ^a
	98.8 ^b	121.8 ^b	36.8 ^b (34.9) ^d	53.5 ^e
		120.8 ^f	32.3 ^g	44.7 ^h

^a Values listed in the API tables ("Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," American Petroleum Institute, Carnegie Press, 1953). ^b Calculated from additivity of group properties (see ref. 9, p. 667). ^c Calculated from difference between butane and 1,3-butadiene (API tables) for the pentane-1,3-pentadiene pair. ^d Calculated from 3-methylhexane (39.9) (API tables) correcting for two π -bonds (2×2.5). ^e Calculated from 3-methylhexane (60.1) (API tables) - (2×4.3) for π -bonds and correcting for the difference between the more reliable value from group properties at 300°K. and the corresponding API value. ^f 121.8 (for 3-methyl-1,5-hexadiene as model compound) + 1.4 for electronic degeneracy - 2.3 for stiffening due to allylic resonance. ^g Using 3-methyl-1,5-hexadiene as a model compound we get 36.8 - 2.0 (eight C-H bending modes) - 2.5 (radical, rotation). ^h 53.5 - 6.4 (eight C-H bending modes) - 2.5 (radical, rotation).

is stereosensitive, we calculate from the measured pressure change ($\sim 1.5\%$ of $(PD)_0$) a maximum effect of 35% on the value of k_5 . The dimerization reaction, however, cannot be the only reason for the scatter in the data of k_5 , as such an effect would show up as a more systematic trend in the variation of k_5 . Different sampling techniques for the quenching of the reaction were used, taking great care not to condense any hydrocarbon together with NO at any time. No effect could be seen. There seems to be no possible way of fractionating our sample before or while the analysis is carried out.

This then leaves us with the conclusion, that all these effects may contribute in part to the scatter of the data. It is unlikely that some uncontrollable side reaction with no net pressure change would have escaped our analysis.

The form of the rate expression is satisfied with consistent k_5 values at a given temperature despite up to 12-fold variation in NO pressure and 3-fold variation in pentadiene pressures. In addition, the results are consistent, starting with either of the isomers. The homogeneity of the reaction has been tested using a packed vessel with an 18-fold greater surface-to-volume ratio and by following the over-all pressure change. If there is any surface activity in the system, the polymerization reaction would become measurably fast (compare experimental part). The results are shown in Table I. Figure 1 shows an Arrhenius plot of the rate constants (units of $\text{mm}^{-1} \text{min}^{-1}$) listed in Table I and yields with standard errors

$$\log k_5 (1./\text{mole sec.}) = (7.26 \pm 0.3) - (18.15 \pm 0.7)/\theta$$

where $\theta = 2.303RT$ (in kcal./mole). Errors calculated from the maximum deviations of limiting slopes are twice as large.

A few kinetic experiments have been carried out with iodine as a catalyst. As mentioned earlier, the reproducibility of these experiments was rather poor, but, despite this, it is obvious that the rates are several hundred times faster than the ones measured with NO.

Discussion

The mechanism for any atom- or radical-catalyzed *cis-trans* isomerization is shown in eq. 1 and has been

discussed earlier.² The rate law for this consecutive-step mechanism, involving formation and internal rotation of an intermediate radical, has been deduced using the steady-state approximation. As a consequence of this reaction mechanism, either the addition

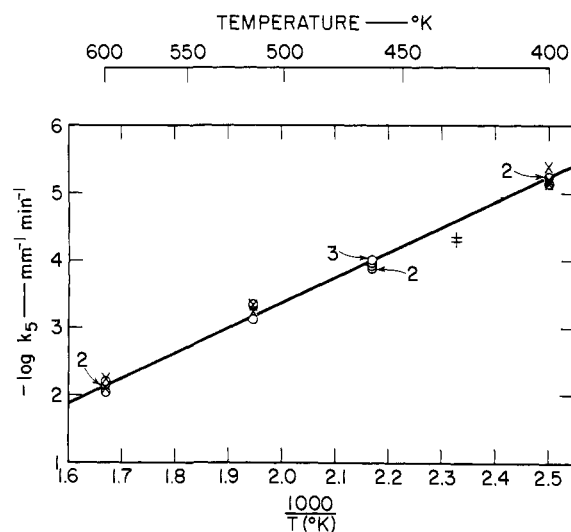


Figure 1. Arrhenius plot of the rate constant for the geometrical isomerization of 1,3-pentadiene. The circles represent data obtained with the *cis* isomer as starting material. Where *trans*-1,3-pentadiene was used, the results are given with \times . (Numbers indicate overlapping points.) Two runs were carried out using a packed vessel (+).

of NO to the double bond (k_a) or the internal rotation about the C-C bond (k_c) in the intermediate adduct radical is the rate-controlling step. It has been shown² that the observed rate constant k_5 should equal $k_c K_{a,b}$ if rotation is the slow step in the system. If the rate is addition controlled, then k_5 can be expected to be within the limits: $0.75k_a > k_5 > 0.25k_a$.

$K_{a,b}$ is estimated, using a value of 11.4 ± 0.7 (standard error) kcal. for $\Delta H^\circ_{a,b}(500^\circ\text{K.})$ ⁸ and other thermodynamic data given in Table II, to be

(8) For details compare Appendix.

Table III. Comparison of Predicted and Experimental Values of k_5 with NO as Catalyst

	Log k_5 , l./mole sec.	Log k_5 (500°K.)
Observed	$(7.3 \pm 0.3) - (18.1 \pm 0.7)/\theta$	-0.6
Addition-controlled rate		
0.25 k_a^a	$(8.7 \pm 0.5) - (14.9 \pm 1.2)/\theta$	$+2.2 \pm 1.0$
Rotation-controlled rate		
$k_c K_{a,b}$	$(7.1 \pm 0.5) - (16.4 \pm 1.7)/\theta$	0.0 ± 1.2

^a 0.25 k_a represents the lowest possible limit. 0.5 k_a would be the expected value to be compared with the observed rate, which would make the difference even more pronounced.

$$K_{a,b} = 10^{-6.2 \pm 0.2} 10^{-11.9 \pm 0.7/\theta} \text{ atm.}^{-1} = 10^{-4.2 \pm 0.2} \times 10^{-12.9 \pm 0.7/\theta} \text{ (l./mole)}$$

(standard errors)

The rotational rate constant k_c has been estimated from transition-state theory³ to be $10^{11.3} 10^{-3.5/\theta}$ sec.⁻¹. From this value of k_c and the estimate of $K_{a,b}$ we can thus predict (k_5') for the case of the rotation-controlled rate

$$\log k_5' = (11.3 \pm 0.5) - (3.5 \pm 1.5)/\theta - (4.2 \pm 0.2) - (12.9 \pm 0.7)/\theta = (7.1 \pm 0.5) - (16.4 \pm 1.7)/\theta$$

This value compares to

$$\log k_5 \text{ (obsd.)} = (7.3 \pm 0.3) - (18.1 \pm 0.7)/\theta$$

k_a is calculated to be $10^{9.3 \pm 0.5} 10^{-14.9 \pm 1.2/\theta}$, using the estimated value for the equilibrium constant $K_{a,b}$ and a value of $10^{13.5 \pm 0.5} 10^{-2 \pm 1/\theta}$ sec.⁻¹ for the back reaction k_b . A value of $10^{13.5}$ for the A factor of the unimolecular bond breaking seems to be a reasonable estimate. There are no directly comparable reliable A factors known, but $\sim 10^{13}$ appears to be a lower limit for unimolecular bond breaking involving splitting of relatively small radicals off larger groups.^{9,10} Any increase in the value for the A factor makes the difference between rotation- and addition-controlled rates even more pronounced. A value of 10^{14} as an upper limit for the A factor is chosen because a higher value would indicate a rather loose complex.

In Table III we compare predicted and experimental rates, and it is apparent that rotation about a single bond is the rate-determining step in the NO-catalyzed *cis-trans* isomerization of 1,3-pentadiene.

Using the observed value for k_5 and the reported estimate for $K_{a,b}$, one can calculate the rotational rate constant $\log k_c$ to be $(11.5 \pm 0.3) - (5.3 \pm 1.0)/\theta$, which compares well (within the error limits) with the values obtained from transition-state theory, from measurements on *cis-trans* isomerization of 2-butene, and other *cis-trans* isomerizations reported in an earlier paper.²

The A factor of 11.5 ± 0.3 is slightly higher than the expected value of 11.2 to 11.3. If we lower the A factor by 0.2 unit to 11.3, this would consequently bring the activation energy for the rotational rate constant from 5.3 kcal. down to 4.2 kcal. The lower value of 4.2 kcal., which corresponds to the barrier to internal rotation, is in even better agreement with the values for

the barrier to rotation in similar molecules, reported from far-infrared studies¹¹: CCl₃CHO (3.0 kcal.), CCl₃CHCH₂ (3.1), CH₃CH₃ (3.0), CH₃CH₂Cl (3.6), etc. A corrected and more reasonable value for the rotational rate constant ($\log k_c^{\text{cor}}$) from this paper would therefore be $\log k_c^{\text{cor}} = 11.3 - 4.2/\theta$, in excellent agreement with the results from the 2-butene isomerization.

As shown in the Appendix, the estimate of $K_{a,b}$ is arrived at using a value of 37 ± 1 kcal. for the C····NO bond strength and 12.6 ± 1 kcal. reported earlier for the allylic resonance energy in the intermediate radical.³ Both these values are further substantiated by the results of this work.

Acknowledgment. We wish to thank David M. Golden for all his stimulating discussions.

Appendix

Estimate of $K_{a,b}$.

$$\Delta H^\circ_{a,b}(500^\circ\text{K.}) = \Delta H^\circ_{a,b}(300^\circ\text{K.}) + 0.2\Delta\bar{C}_p^\circ_{300/500}$$

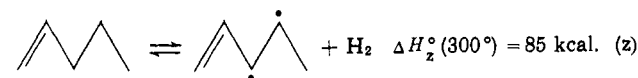
$$\Delta H^\circ_{a,b}(300^\circ\text{K.}) = D(\pi)(300^\circ\text{K.}) \left[\text{Diagram of allylic radical} \right] -$$

$$D(300^\circ\text{K.}) [\text{C} \cdots \cdots \text{NO}] - \text{allyl resonance} = 61 (\pm 0.5) - 37 (\pm 1.0) - 12.6 (\pm 1.0) = 11.4 \pm 1.5 \text{ kcal.}$$

where D is the dissociation energy, and errors are in maximum deviation. The allyl resonance value was obtained from earlier measurements, and the value for $D[\text{C} \cdots \cdots \text{NO}]$ is a tested, judicious guess.³ The D value for the secondary π -bond strength in 1,3-pentadiene (neglecting allylic resonance) is obtained using the heat of reactions y and z



For pentadiene a value of 19.0 kcal. for $\Delta H_f^\circ(300^\circ\text{K.})$ was used.^{7,12-14}



(11) H. G. Silver and J. L. Wood, *Trans. Faraday Soc.*, **59**, 588 (1963).

(12) F. M. Fraser and E. J. Prosen, *J. Res. Natl. Bur. Std.*, **54**, 143 (1955).

(13) Assuming the same value as in propane; see ref. 2.

(14) "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," American Petroleum Institute, Carnegie Press, Pittsburgh, Pa., 1953.

(9) S. W. Benson, "The Foundations of Chemical Kinetics," McGraw-Hill Book Co., Inc., New York, N. Y., 1960, Table XI.5, p. 262.

(10) J. A. Kerr and A. F. Trotman-Dickenson, *Progr. Reaction Kinetics*, **1**, 119 (1961), Table 8.

This value is derived using 94.5 kcal.¹³ for a secondary C-H bond and 104.0 kcal.¹⁴ for H-H.

ΔC_p° for the reaction is calculated using the data for the specific heats listed in Table II. The heat capacity for the NO adduct radical is estimated, using 3-methyl-1,5-hexadiene as a model compound and correcting for the loss of eight C-H bending modes (each contributes 0.25 gibbs/mole at 300°K. and 0.8 gibbs/mole at 500°K.) and a decrease in rotation (~ 2.5 gibbs/mole) due to the generation of an allylic resonance in the radical. This leads to $\Delta C_p^\circ_{a,b} = 2.5$ gibbs/mole and

$$\Delta H^\circ_{a,b}(500^\circ) = 11.4 + 0.5 = 11.9 \pm 0.7 \text{ kcal. (standard error)}$$

$\Delta S^\circ_{a,b}(500^\circ) = -28.2 \pm 1.0$ gibbs/mole is calculated using the entropy data given in Table II. 3-Methyl-1,5-hexadiene is used as a model compound for the radical, adding 1.4 gibbs/mole for the electronic degeneracy in the radical and taking into account a loss in entropy (2.3 gibbs/mole) owing to the stiffening effect of the allylic resonance.

An Electron Spin Resonance Study of Some Complexes of Iron, Nitric Oxide, and Anionic Ligands

C. C. McDonald, W. D. Phillips, and H. F. Mower

Contribution No. 1073 from the Central Research Department, Experimental Station, E. I. du Pont de Nemours and Company, Wilmington, Delaware.
Received March 20, 1965

Paramagnetic species are produced from reaction of nitric oxide with ferrous iron in aqueous solutions containing one or more of a wide variety of additional coordinating species (e.g., hydroxyl, phosphate, arsenate, and molybdate ions, phenol, benzoic acid, β -mercaptoethanol, cysteine). The paramagnetic species exhibit intense e.s.r. spectra with g values in the range from 2.02 to 2.04. The line widths of the resonances are sufficiently narrow in most instances to permit resolution of hyperfine splitting from a variety of magnetic nuclei in the complexes. For example, analysis of the Fe^{57} , N^{14} , N^{15} , and P^{31} hyperfine splittings of the complex formed from reaction of Fe(II), NO, and phosphate indicates that the complex consists of one iron atom, two NO groups, and two phosphate ions. A structure is proposed that involves a tetrahedral distribution of the four coordinating groups about iron. Similar structures are indicated from the e.s.r. spectra for the complexes formed with the other coordinating species mentioned above. Pyrophosphate and adenosine diphosphate appear to act as bidentate ligands in complexes involving iron and NO, while adenosine monophosphate behaves in the same fashion as phosphate ion. Dependences of e.s.r. intensities on complexing ligand concentrations suggest that many of the paramagnetic complexes exist in equilibrium with a diamagnetic complex involving two iron atoms which are antiferromagnetically coupled. Paramagnetic species formed in neutral aqueous solutions from Fe(II) (or Fe(III)), NO, and dithiols also exhibit strong e.s.r. spectra with g values from 2.02 to 2.04. The hyperfine structures of these spectra indicate coordination of one NO molecule and four sulfur atoms about one iron atom. The Fe^{57} and N^{14} splittings depend on the number of atoms in the chelate ring formed by the dithiol. The formal valence state of iron in all of the paramagnetic species reported here appears to be Fe(I).

Introduction

Complexes between iron and nitric oxide occupy a particularly honorable and ancient niche in the history and development of chemistry. Studies of such complexes extend back to Priestley,¹ and the complexes continue to furnish examples of new structures and modes of binding even to this date.²

Recently, complexes of iron and nitric oxide have also assumed some biological significance. Dobry-Duclaux has shown^{3,4} that black Roussin's salt $\{[Fe_4S_3(NO)_7]K\}$ effectively inhibits the enzyme alcohol dehydrogenase at very low concentrations ($\sim 1 \times 10^{-7}$ M). Gordy and Rexroad⁵ demonstrated that complexes of nitric oxide with hemoglobin and cytochrome-c exhibited electron spin resonance (e.s.r.) spectra that could be employed to elucidate the electronic structures of the iron atoms in these biologically important molecules.

Here, we present the results of an investigation by e.s.r. spectroscopy of complexes formed in aqueous solutions from Fe(II), NO, and a variety of inorganic and organic ligands. In most instances, these paramagnetic complexes exhibit e.s.r. spectra with well-resolved nucleus-electron isotropic hyperfine structure. Analyses of these spectra have provided considerable new information regarding the nature of iron-nitric oxide complexes.

(1) J. Priestley, "Experiments and Observations on Different Kinds of Air," Vol. I, Thomas Pearson, Birmingham, 1790, p. 328.

(2) W. P. Griffith, J. Lewis, and G. Wilkinson, *J. Chem. Soc.*, 3993 (1958).

(3) A. Dobry-Duclaux, *Biochim. Biophys. Acta*, **39**, 33 (1960).

(4) A. Dobry-Duclaux, *ibid.*, **39**, 44 (1960).

(5) W. Gordy and H. N. Rexroad in "Free Radicals in Biological Systems," M. S. Blois, Jr., H. W. Brown, R. M. Lemmon, R. O. Lindblom, and M. Weissbluth, Ed., Academic Press Inc., New York, N. Y., 1961, pp. 268-273.