

side of the N-C<sub>1</sub> bond. Supposing that the present iodine complex has a similar configuration, it seems reasonable that the electron-donor orbital of the oxygen is a hybrid of 2p with some 2s, just as for the dioxane-halogen complex as discussed by Mulliken.<sup>35</sup>

*Acknowledgments.* The author wishes to express his sincere thanks to Professor R. S. Mulliken for giving

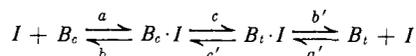
him the opportunity to work at the University of Chicago and for his interest, various suggestions, and reading of the manuscript. He also wishes to thank Dr. M. L. Ginter and other members of the spectroscopic laboratory for helpful advice in the experimental work and for their hospitality. Financial support from the National Science Foundation is gratefully acknowledged.

## Iodine-Catalyzed Isomerization of Olefins. III. Kinetics of the Geometrical Isomerization of Butene-2 and the Rate of Rotation About a Single Bond

Sidney W. Benson, Kurt W. Egger, and David M. Golden

Contribution from the Stanford Research Institute, Menlo Park, California.  
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The kinetics of the gas phase, I<sub>2</sub>-catalyzed geometric isomerizations of *cis*- or *trans*-butene-2 (B<sub>c</sub>, B<sub>t</sub>) have been studied over the temperature range 410 to 520°K. The rate law has the form  $-d(B_c)dt = k(B_c)(I_2)^{1/2} [1 - (B_t)/K_{e,q}(B_c)]$  which is shown to be consistent with the consecutive-step mechanism involving I atom addition to the π-bond.



From an analysis of the steady-state rate for this system and reasonably good estimates of the various rate constants in the scheme, it is shown that the rate-determining slow step in the system is *c* (or *c'*), the rotation about a single bond in the radicals B<sub>c</sub>·I (or B<sub>t</sub>·I). From the observed rate constant *k*<sub>obsd</sub> and an estimate of the equilibrium constant K<sub>a,b</sub> it is found that the rotational rate constant *k*<sub>c</sub> equals 10<sup>11.2</sup> × 10<sup>-3.3/θ</sup> sec.<sup>-1</sup> (where θ = 2.303RT in kcal./mole). This compares well with the value estimated from transition state theory and bond energies, *k*<sub>c(est.)</sub> = 10<sup>11.3</sup> × 10<sup>-3.5/θ</sup> sec.<sup>-1</sup>. These appear to be the maximum rate constants ever measured for a chemical change. By thermodynamic and kinetic analysis of the data on other *cis-trans* isomerizations, both catalyzed and uncatalyzed, it is shown that a similar mechanism may be used to estimate the rates. From the data on the NO-catalyzed isomerizations it may be deduced that the C-N bond dissociation energy in alkyl nitroso compounds is about 37 kcal. Rate constants in gas phase and solution appear to be very similar.

### Introduction

I<sub>2</sub> has long been recognized as one of the extremely effective catalysts for the *cis-trans* isomerization of olefins. Where rate studies have been made, the rate law generally follows the form, rate ∝ (I<sub>2</sub>)<sup>1/2</sup>(olefin).

The appearance of the half-order dependence on I<sub>2</sub> has been interpreted as involving an I atom addition to the olefin as part of the mechanism. If this radical mechanism is correct, then the rate-determining step could be either the rate of internal rotation of the two

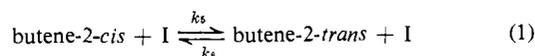
groups in the radical or else the actual addition of the I atom to the olefin. The former possibility is a rather interesting one since it would provide for the first time the prospect of observing the rate of rotation around a single bond as the rate-determining step in a chemical reaction. In the present paper we shall report our kinetic studies of the I<sub>2</sub>-catalyzed isomerizations of butene-2 in the gas phase in which we find that the rate-determining step is indeed the rate of rotation about a single bond. In the final sections we shall also discuss a number of related studies by other authors on *cis-trans* isomerizations, both catalyzed and uncatalyzed, and show that they follow a similar radical pathway.

### Experimental

Very briefly the study consisted of mixing I<sub>2</sub> vapor and *cis*- or *trans*-butene-2 vapor in the gas phase in a thermostated glass reaction vessel in the absence of light and then after predetermined periods of time quenching the entire reaction and analyzing the products. The method used was a variation of that employed by Benson, *et al.*,<sup>1,2</sup> in their studies of the butene-1-butene-2 isomerization and has been reported on in detail earlier.<sup>3a,b</sup> The *cis-trans* isomerization is the fastest reaction in the system and can be carried out at temperatures where the positional isomerization is negligibly slow.

### Results

For the reaction



the rate expression is

$$-\frac{d(B_c)}{dt} = k_5(B_c)(I) \left( 1 - \frac{(B_t)}{K_{5,6}(B_c)} \right) \quad (2)$$

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

(2) S. W. Benson, A. N. Bose, and P. S. Nangia, *ibid.*, **85**, 1388 (1963).

(3) (a) D. M. Golden, K. W. Egger, and S. W. Benson, *ibid.*, **86**, 5416 (1964), part I of this series; (b) *ibid.*, **86**, 5420 (1964), part II.

Table I. Kinetic Data for the *cis-trans* Isomerization of Butene-2

Temp., °K.	Time, min.	[I <sub>2</sub> ] <sub>0</sub> , mm.	[I <sub>2</sub> ] <sub>eff.</sub> <sup>a</sup> , mm.	[B] <sub>0</sub> <sup>b</sup> , B <sub>t</sub> , B <sub>c</sub> <sup>b</sup> , mm.	K <sub>1,2</sub> × 10 <sup>6</sup> , mm.	K <sub>5,6</sub>	B <sub>t</sub> /B <sub>c</sub>	k <sub>5</sub> , min. <sup>-1</sup> mm. <sup>-1</sup>
410.8	1358	24.8	23.3	c 41.6	2.810	2.31	0.449	22.3
	1308	25.0	23.7	c 129.3				18.3
	1084	24.2	23.0	c 55.6				20.3
410.1	341	26.5	26.0	c 35.1	2.707	2.32	0.103	21.1
410.0	1317	25.3	24.1	c 154.9	2.714	2.32	0.313	16.1
411.1	360	33.6	33.0	c 64.9	2.868	2.31	0.109	17.9
432.4	160.5	44.0	43.0	c 81.1	8.630	2.15	0.157	16.8
431.4	233	24.0	23.7	c 118.4	8.194	2.16	0.143	15.2
	126	34.1	33.4	c 78.3				17.6
430.8	232	34.9	34.2	t 80.8	7.980	2.16	11.02	19.5
446.4	144	39.3	38.5	c 75.1	16.90	2.08	0.309	19.1
	142	34.5	33.7	c 46.4				19.7
	86	41.9	41.0	t 96.6				22.8
465.3	40	25.1	24.1	c 40.9	38.76	1.90	0.238	30.1
	40	26.0	25.3	c 40.7				29.6
	20	4.0	3.8	c 30.3				32.8
	20	4.0	3.9	c 34.4				32.8
	171	23.3	22.9	t 36.3				28.8
	92	24.3	23.9	t 35.5				26.7
	45	24.6	24.3	t 32.9				30.1
466.3	40	30.6	30.1	c 39.2	40.62	1.91	0.279	32.3
467.7	42	25.9	25.2	c 45.2	43.12	1.93	0.309	30.0 <sup>c</sup>
502.4	17.6	4.8	4.6	c 47.6	168.2	1.79	0.359	53.4
	9.2	4.4	4.2	c 86.1				56.4
	13.3	4.8	4.4	c 182.0				53.4
	26.3	4.9	4.5	t 55.5				62.1
502.0	14.3	10.3	10.1	t 34.9	165.3	1.80	5.04	53.8
519.1	9.8	4.9	4.4	t 91.9	302.5	1.73	3.88	84.1
	15.3	4.4	3.8	t 75.6				86.8
	8.3	5.6	5.4	t 64.1				80.2
	10.3	9.3	8.7	c 66.2			0.711	74.0

<sup>a</sup> Effective iodine pressures, calculated from the initial iodine pressures [I<sub>2</sub>]<sub>0</sub> correcting for changes in iodine pressure during the reaction (see ref. 3b). <sup>b</sup> B<sub>t</sub> and B<sub>c</sub> stand for butene-2-*trans* and butene-2-*cis*, respectively. <sup>c</sup> Packed vessel.

and yields upon integration

$$k_5 = \frac{-K_{5,6}/(K_{5,6} + 1)}{K_{1,2}^{1/2}[I_2]^{1/2}t} \ln \left[ \left( \frac{B_c}{B_c^0} \right) - \frac{1}{1 + K_{5,6}} \right] \times \left( \frac{K_{5,6} + 1}{K_{5,6}} \right) \quad (3)$$

where  $K_{5,6}$  is the equilibrium constant equal to  $k_5/k_6$ ,<sup>3</sup>  $K_{1,2}^{1/2}[I_2]^{1/2}$  is the pressure of I atoms,<sup>4</sup> and  $(B_c)/(B_c^0)$  is the ratio of butene-2-*cis* in the products to the initial amount of butene. If butene-2-*trans* is used as the starting material,  $k_6$  is calculated and  $k_5$  is obtained from the equilibrium constant.

Table I contains values for the rate constant  $k_5$  obtained from eq. 3 over a temperature range from 410 to 520°K. From the consistency of  $k_5$  at the various temperatures, despite as much as fourfold variation in butene pressure and as much as sixfold variation in iodine pressure, it is seen that the form of the rate expression is satisfactory. Further indication of this is offered by the fact that  $k_5$  measured from  $k_6$  and  $K_{5,6}$  is consistent with  $k_5$  directly measured.

The homogeneity of the reaction was tested with only one run in a vessel with an 18-fold greater surface to volume ratio than the normal vessel. No effect whatsoever was detected at 468°K. which is in the middle of the temperature range studied here. Extensive tests of the homogeneity of the positional isomerization of butene were carried out in the same system<sup>3b</sup> and showed no surface effects.

(4)  $K_{1,2}$  values taken from "JANAF Interim Thermochemical Tables," D. R. Shull, Ed., Dow Chemical Co., Midland, Mich., 1963.

Figure 1 shows an Arrhenius plot of the rate constants listed in Table I (units of mm.<sup>-1</sup> min.<sup>-1</sup>). Changing to concentration units, log  $k_5$  (l./mole sec.) =

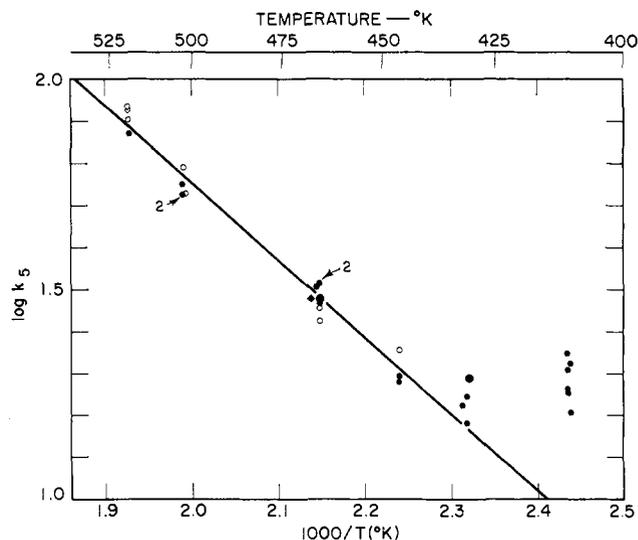


Figure 1. Kinetics of the *cis-trans* isomerization of butene-2. Plot of the log  $k_5$  (units of mm.<sup>-1</sup> min.<sup>-1</sup>) values, listed in Table I, vs.  $1/T$  (in °K.): the solid points represent data obtained with butene-2-*cis* as starting material; for other values butene-2-*trans* was used (◊, run in packed vessel).

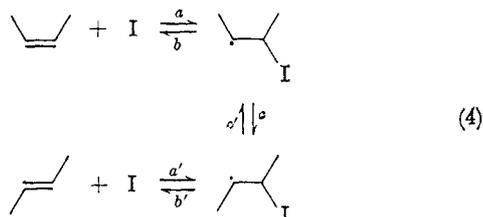
$(8.50 \pm 0.30) - (9.4 \pm 0.6)/\theta$  (expected error) (the errors calculated from the maximum deviations of

limiting slopes are  $\pm 0.60$  for the  $A$  factor and  $\pm 1.3$  for the activation energy), and  $\theta = 2.303RT$  in kcal./mole.

The low temperature points at about 410 and 430°K. deviate from the Arrhenius line probably owing to the increasing stability of iodides at these temperatures. From 450 to 520°K. the data fit an Arrhenius line very well.

### Discussion

The mechanism for iodine atom catalyzed *cis-trans* isomerization of butene-2 is



Assuming that the intermediate radicals are present in steady-state concentrations, we derive the rate law

$$-\frac{d(\text{B}_c)}{dt} = \frac{K_{a,b}k_c(\text{B}_c)(\text{I})}{1 + K_{c,b} + K_{c',b'}} \left( 1 - \frac{k_{c'}K_{a',b'}(\text{B}_t)}{k_cK_{a,b}(\text{B}_c)} \right) \quad (5)$$

where  $k_a/k_b = K_{a,b}$ , etc. Comparison of (2) and (5) yields the relations

$$k_5 = \frac{K_{a,b}k_c}{1 + K_{c,b} + K_{c',b'}} \quad (6a)$$

$$K_{5,6} = \frac{k_{c'}K_{a',b'}}{k_cK_{a,b}} \quad (6b)$$

While it is possible to calculate  $k_5$  for reactions of the type 4 from available thermodynamic and kinetic data, it is of interest to note that the expression for  $k_5$  reduces in the following three possible cases.

Case I

$$K_{c,b} \text{ and } K_{c',b'} \ll 1 \\ k_5 = K_{a,b}k_c \quad (7)$$

Case II

$$K_{c,b} \text{ and } K_{c',b'} \gg 1 \\ k_5 = \frac{K_{a,b}k_c}{K_{c,b} + K_{c',b'}} = \frac{k_bK_{a,b}K_{c,c'}}{1 + K_{c,b}/K_{c',b'}} \quad (8)$$

The ratio  $K_{c,b}/K_{c',b'}$  is most likely to fall in the range  $1/3$  to 3, as the relative stabilities of the "cis" and "trans" radicals are not radically different. Then

$$\frac{1}{4}k_a < k_5 < \frac{3}{4}k_a \quad (9)$$

Case III

$$K_{c,b} \approx K_{c',b'} \sim 1 \\ k_5 = \frac{k_bK_{a,b}K_{c,c'}}{1 + \frac{K_{c,b}}{K_{c',b'}} + \frac{1}{K_{c',b'}}} \sim \frac{1}{3} k_bK_{a,b}K_{c,c'} \sim \frac{1}{3} k_a \quad (10)$$

The equilibrium constant  $K_{a,b}$  (470°K.) is estimated from the thermodynamic data given in Table II (and  $\Delta C_p^\circ \sim 3$  e.u.) to be  $K_{a,b} = 10^{-4.9}10^{-4.5/\theta}$  atm.<sup>-1</sup> =  $10^{-2.9}10^{-5.5/\theta}$  l./mole. The following value is estimated

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

Species	$S^\circ$ , e.u.	$\Delta H_f^\circ$ , kcal./mole
I	43.2 <sup>a</sup>	25.5 <sup>a</sup>
B <sub>c</sub>	71.9 <sup>a</sup>	-1.7 <sup>a</sup>
B <sub>t</sub>	70.9 <sup>a</sup>	-2.7 <sup>a</sup>
sec-Butyl iodide	91.1 <sup>b</sup>	28.9 <sup>c</sup>
$\Delta S_{a,b}^\circ = -24$ e.u.		$\Delta H_{a,b}^\circ = +5$
$\Delta S_{a',b'}^\circ = -23$ e.u.		$\Delta H_{a',b'}^\circ = +6$

<sup>a</sup> S. W. Benson, "The Foundations of Chemical Kinetics," McGraw-Hill Book Co., Inc., New York, N. Y., 1960, p. 662. <sup>b</sup> Calculated from a value of 89.8 for *sec*-butyl iodide + 1.3 e.u. for the radical taking into account a loss of H and a gain from electronic degeneracy: see S. W. Benson and A. N. Bose, *J. Chem. Phys.*, **39**, 3463 (1963). <sup>c</sup> Calculated from values for *sec*-butyl iodide, H atoms, and a bond strength of 95 kcal. (see footnote b).

for  $k_a$ :  $k_a \sim 10^{8.1}10^{-6.5/\theta}$  atm.<sup>-1</sup> sec.<sup>-1</sup> or  $\sim 10^{10.1}10^{-7.5/\theta}$  l./mole sec.

The value of  $10^{8.1}$  atm.<sup>-1</sup> sec.<sup>-1</sup> for the  $A$  factor is arrived at by combining the value for the entropy  $\Delta S_{a,b}^\circ$  (470°K.) = -22.6 e.u. calculated above and a value for the  $A$  factor of reaction  $b$ , which is unimolecular bond breaking, of  $10^{13}$  sec.<sup>-1</sup>. If the  $A$  factor of reaction  $b$  differs from  $10^{13}$  sec.<sup>-1</sup>, it probably is not lower by as much as  $10^1$ , which would set a lower limit on the  $A$  factor of reaction  $a$  of  $10^{7.1}$  atm.<sup>-1</sup> sec.<sup>-1</sup>. If the value of the entropy  $\Delta S_{a,b}^\circ$  were lower by 2 e.u., the  $A$  factor of reaction  $a$  might be further lowered to  $\sim 10^{6.7}$ , but this is unlikely.

The activation energy of 6.5 kcal. is derived from the fact that the heat of reaction  $\Delta H_{a,b}^\circ$  (470°K.) is +4.5 kcal./mole, and therefore the activation energy of reaction  $a$  must be 4.5 kcal./mole plus the activation energy of  $b$ .

The activation energy of reaction  $b$  is estimated at about 2 kcal./mole to conform with expectations for the activation energy for I atom attack on double bonds. This means that  $k_b = 10^{13}10^{-2/\theta}$  sec.<sup>-1</sup>.

The rate constant  $k_c$  is calculated from the transition state formula

$$k_c = \frac{RT}{h} K_c^* e^{-E_0^*/RT} \quad (11)$$

The use of eq. 11, which implies that the *sec*-butyl iodide radicals formed in step  $a$  are in equilibrium with the transition state for rotation, is justified by the fact that for  $K_{c,b} \sim K_{c',b'} \ll 1$  (i.e., case I) the steady-state concentration of radicals is the same as if they were in equilibrium with the reactants. Since the transition state theory requires that the reactants and transition state complex be in equilibrium, then by detailed balancing, the radicals are also in equilibrium with the transition state.

Where case I does not apply,  $k_c$  is uninteresting.

The transition state complex for the isomerization corresponds to the eclipsed form of the radical if we assume tetrahedral geometry. If the radical is assumed planar, it corresponds to a configuration in which the CH<sub>3</sub> group attached to the radical end is 30° away from the CH<sub>3</sub> group on the adjacent C atom. There is evidence which is believed to favor the planar structure.<sup>5</sup>

(5) S. W. Benson, D. M. Golden, and K. W. Egger, *J. Chem. Phys.*, to be published.

If we assume that the vibrational modes are not significantly different in passing to the transition state and that the rotational partition function is also not very different, then  $(K_c^*)^{-1} = Q_{\text{int}}^*$  equals the partition function for hindered internal rotation in the *cis* (or *trans*) form of the radical. But this is<sup>6</sup>

$$Q_{\text{int}} = (8\pi^3 IRT/h^2)^{1/2} \quad (12)$$

so that on substitution

$$k_c = \frac{1}{2\pi} \left( \frac{RT}{2\pi I} \right)^{1/2} e^{-E_0^*/RT} \quad (13)$$

which has the form

$$k_c = A'T^{1/2}e^{-E_0^*/RT} \quad (14)$$

This may be written in the Arrhenius form (with a mean temperature of  $\sim 500^\circ\text{K}$ .) as

$$k_c = A'10^{1.6}10^{-(E_0^*+0.5)/\theta} \quad (15)$$

The moment of inertia  $I$  is calculated for the rotation of the ethylidene radical about the C–C bond as if the iodine-containing end of the radical were an infinite mass. This leads to a value of  $A = A'10^{1.6} = 10^{11.3} \text{ sec.}^{-1}$ .

Since  $E_0^*$  is the difference in ground-state energies of reactant and transition state, it should correspond to the barrier to internal rotation. From the values for similar molecules (*i.e.*,  $\text{CCl}_3\text{CHO}$ ,  $\text{CH}_3\text{CH}_3$ ,  $\text{CCl}_3\text{CHCH}_2$ ),<sup>7</sup> it would seem that 3 kcal./mole would be a reasonable figure for the barrier here. Thus we estimate  $k_c = 10^{11.3}10^{-3.5/\theta} \text{ sec.}^{-1}$ . Then,  $K_{c,b} = 10^{11.3}10^{-3.5/\theta}/10^{13}10^{-2/\theta} = 10^{-1.7}10^{-1.5/\theta} \ll 1$ . Since  $K_{c',b'}$  is not expected to differ greatly from  $K_{c,b}$ , case I applies and  $k_5 = k_c K_{a,b} = 10^{8.4}10^{-9.0/\theta} \text{ l./mole sec.}$ , in excellent agreement with the experiment.

If the estimate of  $k_c$  is far off, so that case II would apply rather than case I, it is seen from (9) that  $10^{9.5} \cdot 10^{-7.5/\theta} < k_5 < 10^{10.0}10^{-7.5/\theta}$ . Case III would be indistinguishable from case II on the basis of kinetic evidence.

Table III offers a comparison of predicted and experimental values. It is then apparent that reaction *c*, a rotation about a single bond, is the rate-determining step.

Table III. Comparison of Predicted and Experimental Values of  $k_5$

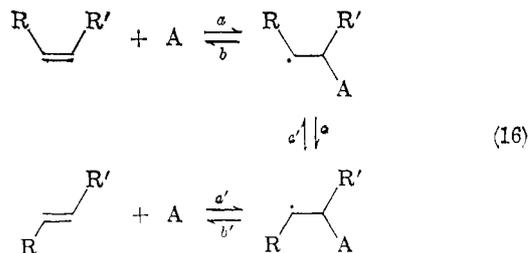
	$k_5$ , l./mole sec.	log $k_5$ at 500°K. ( $\theta = 2.3$ )
Case I, $k_5 = k_c K_{a,b}$	$10^{8.4}10^{-9.0/\theta}$	4.5
Case II, $k_5 = 1/4 k_a$ (reasonable lower limit)	$10^{9.5}10^{-7.5/\theta}$	6.2
Case III: $k_5 = 1/3 k_a$	$10^{9.6}10^{-7.5/\theta}$	6.3
Experimental value	$10^{(8.5 \pm 0.3)}10^{-(9.4 \pm 0.6)/\theta}$	4.4

### Other Catalyzed *cis-trans* Isomerizations

For any atom or radical catalyzed *cis-trans* isomerization the mechanism offered in (4) may be generalized

(6) K. S. Pitzer, "Quantum Chemistry," Prentice-Hall, Inc., New York, N. Y., 1953.

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



If the bond strength of the secondary C–A bond and any resonance energy introduced by R add up to 58 kcal./mole or more (the approximate strength of the C=C double bond in the absence of resonance effects), the rotation will be faster than either addition or removal of A and will not be rate controlling. Calculations can be carried out the same way as has been shown for the I atom catalyzed *cis-trans* isomerization of butene-2.

If A can be produced from  $A_2$  by both thermal and photochemical means, the difference in activation energies for an isomerization carried out both ways should be equal to one-half the bond strength of the A–A bond if the atomic mechanism is correct. This is indeed the case.

To test the compatibility of the mechanism in (16) with experiment, values of  $K_{a,b}$  have been estimated for several catalyzed isomerizations listed by Cundall,<sup>8</sup> and these are tabulated in Tables IVa and IVb. Where rotation is rate determining (case I),  $k_c$  is calculated from the observed rate constant. Where rotation is not rate controlling (case II or III), observed rate constants are compared to values of  $k_a$  (exchange rate constants should be equal to  $1/2 k_a$ ).

While the comparison with gas phase data is straightforward, the comparisons with solution data are subject to some uncertainties owing to differences in energies and entropies of solution. For nonpolar systems these are not expected to be large.

It is seen from Table IVa that the  $k_c$  values, calculated from observed rate constants by dividing by estimated values of  $K_{a,b}$ , are generally of the order of magnitude expected. The NO-catalyzed isomerizations fit the mechanism quite well. The values of  $k_c$  from 4a, 5a, and 6a of Table IVa agree with expectations, although log  $A$  and  $E$  are both larger than expected. The uncertainty in the observed data may account for the discrepancy in the Arrhenius parameters.

Table IVb illustrates the remarkably good agreement between estimates of  $k_a$  and the observed rate constants for addition-controlled isomerization and halogen atom exchange. In the case of *cis-stilbene* (1a), the  $A$  factors agree quite well, but the estimate of the activation energy  $E_a$  cannot be narrowed further. In 2b the assignment of  $E_a = 0$  comes from the results of 5b which force this conclusion. The exchange rate constants 3b, 4b, and 5b are in excellent agreement with one-half the estimated  $k_a$ .

### Uncatalyzed *cis-trans* Isomerizations

The possibility that rotation about a single bond is rate controlling exists for the thermal *cis-trans* isomerization of olefins as well as for the catalyzed isomeri-

(8) R. B. Cundall, "Progress in Reaction Kinetics," Vol. 2, The Macmillan Co., New York, N. Y., 1964, Chapter 4.



Table V. Rate Constants for Thermal *cis-trans* Isomerization<sup>a</sup>

Compound	State	Log <i>A</i> , sec. <sup>-1</sup>	<i>E</i> , kcal./mole	Source	Mean Temp., °K.
1 <i>cis</i> -Butene-2	Gas	13.8	62.8	<i>b</i>	690
		14	62.4	<i>c</i>	
		(13.0)	(61)	<i>d</i>	
2 <i>trans</i> -Dideuterioethylene	Gas	13	65		770
		(14.1)	(64)		
3 <i>cis</i> -Stilbene	Gas	12.8	42.8	<i>e</i>	580
		(10.9)	(33.5)		
4 <i>cis</i> -Methyl cinnamate	Gas	10.5	41.6	<i>f</i>	610
		(11.9)	(42)		
5 β-Cyanostyrene	Gas	11.6	46.0	<i>g</i>	610
		(11.9)	(46)		
6a <i>cis</i> -Stilbene	Liquid <sup>h</sup>	10.4	36.7	<i>i</i>	500
		(10.9)	(33.5)		
6b <i>cis</i> -Chlorostilbene	Liquid <sup>j</sup>	11.1	37	<i>k</i>	490
6c <i>cis</i> -Dichlorostilbene	Liquid <sup>j</sup>	11	34	<i>k</i>	460
6d <i>cis-p</i> -Methoxystilbene	Liquid <sup>j</sup>	10.2	35.5	<i>k</i>	560
6e <i>cis-p</i> -Nitrostilbene	Liquid <sup>j</sup>	10.2	34	<i>k</i>	510
6f Ethyl α-bromoallo-cinnamate	Liquid <sup>j</sup>	11.1	39.2	<i>l</i>	530
6g Methyl <i>o</i> -methoxy-allo-cinnamate	Liquid <sup>j</sup>	9.8	39.4	<i>l</i>	540

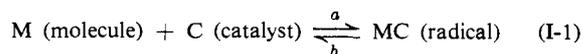
<sup>a</sup> Predicted values in parentheses; the predictions are discussed in Appendix II. <sup>b</sup> B. S. Rabinovitch and K. W. Michel, *J. Am. Chem. Soc.*, **81**, 5065 (1959). <sup>c</sup> R. B. Cundall and T. F. Palmer, *Trans. Faraday Soc.*, **57**, 1936 (1961). <sup>d</sup> J. E. Douglas, B. S. Rabinovitch, and F. S. Looney, *J. Chem. Phys.*, **23**, 315 (1955); **20**, 1952 (1952). <sup>e</sup> G. B. Kistiakowsky and W. R. Smith, *J. Am. Chem. Soc.*, **56**, 638 (1934). <sup>f</sup> G. B. Kistiakowsky and W. R. Smith, *ibid.*, **57**, 269 (1935). <sup>g</sup> G. B. Kistiakowsky and W. R. Smith, *ibid.*, **58**, 2428 (1936). <sup>h</sup> The fact that all liquid results are in different solvents (*i.e.*, pure liquid) means that kinetic parameters are hard to compare. <sup>i</sup> T. W. T. Taylor and A. R. Murray, *J. Chem. Soc.*, 2078 (1938). <sup>j</sup> Thermodynamic data upon which to base predictions are not available, but similarity to *cis*-stilbene seems to indicate that substituents do not have much of an effect. <sup>k</sup> M. Calvin, and H. W. Alder, *J. Chem. Phys.*, **19**, 768 (1951). <sup>l</sup> M. Davies and F. P. Evans, *Trans. Faraday Soc.*, **51**, 1506 (1955).

While there is no unequivocal proof of the existence of a flat biradical state in olefins, there are indications of triplet states in the right energy region. Evans<sup>10a</sup> has seen oxygen perturbed singlet-triplet absorption bands in ethylene, dideuterioethylene, and tetra-deuterioethylene. Grabowski and Bylina<sup>10b</sup> have observed the same sort of transitions in 1,2-dichloroethylene.

The rate constants and equilibrium constants estimated for the *cis-trans* isomerization of butene-2 are based on well-known thermodynamic data. In some of the cases of Tables IV and V the uncertainties are somewhat larger. Nevertheless, it seems quite clear that the mechanism discussed here is adequate to explain most of the available data. Nowhere is it necessary to distinguish between singlet and triplet intermediates, biradical and radical intermediates being sufficient to account for the observations.

### Appendix I

Estimation of  $K_{a,b}$  and  $k_a$  for Catalyzed Isomerization. Labeling reactions *a* and *b* of (16) as



the estimated equilibrium constants and rate constants tabulated in Table IV of the text are arrived at as follows.

$$(1a) S^{\circ}_{600} (M) = S^{\circ}_{600} (\text{ethylene})^{11} + (0.7/D)^{12} + R \ln 2 = 64.7 \text{ e.u.}$$

(10) (a) D. F. Evans, *J. Chem. Soc.*, 1735 (1960); (b) Z. R. Grabowski and A. Bylina, *Trans. Faraday Soc.*, **60**, 1131 (1964).

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

(12) Footnote *a* of Table II.

$$S^{\circ}_{600} (C) = 55.4 \text{ e.u.}^{11}$$

$$S^{\circ}_{600} (MC)^{13} = S^{\circ}_{600} (\text{butene-1})^{11} + R \ln \sigma (\text{butene-1}) + 10.7/D + R \ln q + R \ln Z (\text{opt. center}) - 3.6^{14} = 95.0 \text{ e.u.}$$

$$\Delta S^{\circ}_{a,b} (600^{\circ}\text{K.}) = -25.1 \text{ e.u.}$$

$$\Delta H^{\circ}_{a,b} (300^{\circ}\text{K.}) = D(\pi) \left( \frac{H}{H} > C \cdots C < \frac{H}{H} \right) - D^{\circ}(C \cdots NO) = 59^{15} - 37^{16} = 22 \text{ kcal./mole}$$

$$\Delta H^{\circ}_{a,b} (600^{\circ}\text{K.}) = \Delta H^{\circ}_{a,b} (300^{\circ}\text{K.}) + \overline{\Delta C^{\circ}}_{pa,b} (600-300^{\circ}\text{K.})$$

$$\overline{C^{\circ}}_p (\text{ethylene}) = 13.8^{11} \text{ e.u.}; \quad \overline{C^{\circ}}_p (C) = 7.3^{11} \text{ e.u.}; \\ \overline{C^{\circ}}_p (\text{butene-1}) = 27.9^{11} \text{ e.u.}$$

$$\overline{C^{\circ}}_p (MC) = \overline{C^{\circ}}_p (\text{butene-1}) - 4^{17} = 23.9 \text{ e.u.}$$

$$\Delta \overline{C^{\circ}}_{pa,b} \sim 3 \text{ e.u.}$$

$$\Delta H^{\circ}_{a,b} (600^{\circ}\text{K.}) = 23 \text{ kcal./mole}$$

$$K_{a,b} (600^{\circ}\text{K.}) = 10^{-5.5} 10^{-23/\theta} \text{ atm.}^{-1} = 10^{-3.4} 10^{-24/\theta} \text{ l./mole}$$

$$(2a) S^{\circ}_{600} (M) = 90.0^{11} \text{ e.u.}; \quad S^{\circ}_{600} (C) = 55.4 \text{ e.u.}^{11}$$

$$S^{\circ}_{600} (MC) = S^{\circ}_{600} (3\text{-methylpentene-1})^{11} + R \ln \sigma (3\text{-methylpentene-1}) + R \ln q - R \ln \sigma (MC) - 3.6^{14} = 121.1 \text{ e.u.}$$

(13) Butene-1 is used as a substitute for the radical since  $-N=O$  is isoelectronic with  $-\text{CH}=\text{CH}_2$  and similar in mass and size. The change to the radical by removal of an H atom adds a term  $R \ln q$  for electronic degeneracy ( $q = 2$ ).

(14) The four extra hydrogens contribute about 3.6 e.u. at 600°K. attributed to an extra eight deformations of about 1200 cm.<sup>-1</sup> each.

(15) See Appendix II.

(16) A judicious guess.

(17) Correction for C-H bending modes.

$$\Delta S^\circ_{a,b} (600^\circ\text{K.}) = -24.3 \text{ e.u.}$$

$$\Delta H^\circ_{a,b} (300^\circ\text{K.}) = D(\pi) \left( \begin{array}{c} \text{CH}_3 \\ | \\ \text{H} \end{array} > \text{C} \cdots \text{C} < \begin{array}{c} \text{CH}_3 \\ | \\ \text{H} \end{array} \right) - D^\circ (\text{C-NO}) = 56^{15} - 37 = 19 \text{ kcal./mole}$$

$$\bar{C}^\circ_p (\text{M}) = 26.4 \text{ e.u.}; \quad \bar{C}^\circ_p (\text{C}) = 7.3 \text{ e.u.}; \\ \bar{C}^\circ_p (\text{3-methylpentene-1}) = 47.3 \text{ e.u.}$$

$$\Delta \bar{C}^\circ_{p,a,b} \sim 13.6 \text{ e.u.} - 4 (\text{corn. for 4H}) = 9.6 \text{ e.u.}$$

$$\Delta H_{a,b} (600^\circ\text{K.}) = 22 \text{ kcal./mole}$$

$$K_{a,b} (600^\circ\text{K.}) = 10^{-5.3} 10^{-22/\theta} \text{ atm.}^{-1} = 10^{-3.2} 10^{-23/\theta} \text{ l./mole}$$

$$(3a) \Delta S^\circ_{a,b} (600^\circ\text{K.}) = -24.3 \text{ e.u. (same as (3))}^{11}$$

$$\Delta H^\circ_{a,b} (300^\circ\text{K.}) = 20 \text{ kcal./mole}$$

$$[D(\pi) \left( \begin{array}{c} \text{H} \\ | \\ \text{CH}_3 \end{array} > \text{C} \cdots \text{C} < \begin{array}{c} \text{CH}_3 \\ | \\ \text{H} \end{array} \right) = 57^{15}]$$

$$\Delta H^\circ_{a,b} (600^\circ\text{K.}) = 22 \text{ kcal./mole} \\ (\Delta \bar{C}^\circ_{p,a,b} \sim 8 \text{ e.u.})^{11}$$

$$K_{a,b} (600^\circ\text{K.}) = 10^{-5.3} 10^{-22/\theta} \text{ atm.}^{-1} = \\ 10^{-3.2} 10^{-23/\theta} \text{ l./mole}$$

$$(4a) S^\circ_{300} (\text{M}) = 78.4 \text{ e.u. (from additivity of bond properties}^{12})$$

$$S^\circ_{300} (\text{C}) = 43.2^{12} \text{ e.u.}$$

$$S^\circ_{300} (\text{MC}) = S^\circ_{300} (\text{MCH}) + R \ln q + \\ (1 \text{ e.u. for increase in internal rotation}) = 98.7 \text{ e.u.}$$

$$S^\circ_{300} (\text{MCH}) = 96.3 \text{ e.u. (from additivity of bond properties}^{12})$$

$$\Delta S^\circ_{a,b} (300^\circ\text{K.}) = -22.9 \text{ e.u.}$$

$$\Delta H^\circ_{a,b} (300^\circ\text{K.}) = D(\pi) \left( \begin{array}{c} \text{I} \\ | \\ \text{H} \end{array} > \text{C} \cdots \text{C} < \begin{array}{c} \text{H} \\ | \\ \text{I} \end{array} \right) - \\ D^\circ (>\overset{\text{I}}{\text{C}}\cdots\text{I}) \\ = 57 (\text{as in butene-2}) - 51 (\text{as in isopropyl iodide}) = 6 \text{ kcal./mole}^{18}$$

$$K_{a,b} (300^\circ\text{K.}) = 10^{-5.0} 10^{-6/\theta} \text{ atm.}^{-1} = \\ 10^{-3.2} 10^{-7/\theta} \text{ l./mole}$$

If  $E_a \sim 8$  kcal./mole (same as for *cis*-butene-2 + I; see text),  $k_a \sim 10^{9.8} 10^{-8/\theta}$  l./mole sec. (since the  $A$  factor for  $k_b \sim 10^{13}$  sec.<sup>-1</sup>)

(5a)  $\Delta S^\circ_{a,b}$  [same as (4a) since bond additivity does not distinguish geometrical isomers]

$$\Delta H^\circ_{a,b} = 5 \text{ kcal./mole, } K_{a,b} (300^\circ\text{K.}) = 10^{-5.0} 10^{-5/\theta} \text{ atm.}^{-1} = 10^{-3.2} 10^{-6/\theta} \text{ l./mole}$$

$$(6a) S^\circ_{300} (\text{M}) = 68.6 \text{ e.u. (from additivity of properties}^{12})$$

$$S^\circ_{300} (\text{C}) = 43.2 \text{ e.u.}^{12}$$

$$S^\circ_{300} (\text{MC}) = S^\circ_{300} (\text{MCH}) + R \ln q + \\ (1 \text{ e.u. for increase in internal rotation}) = 88.8 \text{ e.u.}$$

(18) There seems to be some evidence that both of these values may be too high by approximately the same amount.

$$S^\circ_{300} (\text{MCH}) = 86.4 \text{ e.u. (from additivity of bond properties}^{12})$$

$$\Delta S^\circ_{a,b} (300^\circ\text{K.}) = -23.0 \text{ e.u.}$$

$$\Delta H^\circ_{a,b} (300^\circ\text{K.}) = 5 \text{ kcal./mole [same as (5a)]}$$

$$K_{a,b} (300^\circ\text{K.}) = 10^{-5.0} 10^{-5/\theta} \text{ atm.}^{-1} = \\ 10^{-3.2} 10^{-6/\theta} \text{ l./mole}$$

$$(1b) S^\circ_{300} (\text{M}) = 108.5 \text{ e.u. (from additivity of bond properties}^{12})$$

$$S^\circ_{300} (\text{C}) = 43.2 \text{ e.u.}^{12}$$

$$S^\circ_{300} (\text{MC}) = S^\circ_{300} (\text{MCH}) + R \ln q = \\ 129.2 \text{ e.u. (rotational increase offset by stiffening of the } \text{C}_6\text{H}_5\text{-C bond for benzylic resonance)}$$

$$S^\circ_{300} (\text{MCH}) = 127.8 \text{ e.u. (from additivity of bond properties}^{12})$$

$$\Delta S^\circ_{a,b} (300^\circ\text{K.}) = -22.5 \text{ e.u.}$$

$$\Delta H^\circ_{a,b} (300^\circ\text{K.}) = D(\pi) \left( \begin{array}{c} \text{C}_6\text{H}_5 \\ | \\ \text{H} \end{array} > \text{C} \cdots \text{C} < \begin{array}{c} \text{C}_6\text{H}_5 \\ | \\ \text{H} \end{array} \right) - \\ D^\circ (\text{sec-C-I}) + \text{benzylic resonance energy} = 30.7 + \\ 14 - 51 = -6 \text{ kcal./mole}$$

$$K_{a,b} (300^\circ\text{K.}) = 10^{-4.9} 10^{6/\theta} \text{ atm.}^{-1} = \\ 10^{-3.0} 10^{5/\theta} \text{ l./mole}$$

If the  $A$  factor for  $k_b \sim 10^{13}$  sec.<sup>-1</sup>  
 $k_a \sim 10^{10.0} 10^{-E_a/\theta}$  l./mole sec.

Since reaction  $a$  is exothermic  $E_a \sim 0-7$  kcal./mole

$$(2b) S^\circ_{300} (\text{M}) = 74.4 \text{ e.u. (from additivity of bond properties}^{12})$$

$$S^\circ_{300} (\text{C}) = 41.8 \text{ e.u.}^{12}$$

$$S^\circ_{300} (\text{MC}) = S^\circ_{300} (\text{MCH}) + R \ln q + 1 \text{ e.u. (for loosening of rotation)} \\ 92.7 \text{ e.u.}$$

$$S^\circ_{300} (\text{MCH}) = 90.3 \text{ e.u. (from additivity of bond properties}^{12})$$

$$\Delta S^\circ_{a,b} (300^\circ\text{K.}) = -23.5 \text{ e.u.}$$

$$\Delta H^\circ_{a,b} (300^\circ\text{K.}) = D(\pi) \left( \begin{array}{c} \text{Br} \\ | \\ \text{H} \end{array} > \text{C} \cdots \text{C} < \begin{array}{c} \text{Br} \\ | \\ \text{H} \end{array} \right) -$$

$$D^\circ (>\overset{\text{Br}}{\text{C}}\cdots\text{Br}) = 57 (\text{as in butene-2}) - 67 (\text{as in isopropyl bromide}) = -10 \text{ kcal./mole}^{19}$$

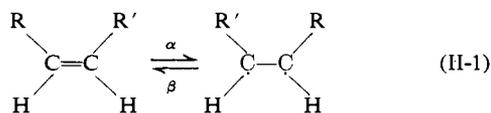
$$K_{a,b} (300^\circ\text{K.}) = 10^{-5.1} 10^{10/\theta} \text{ atm.}^{-1} = 10^{-3.2} 10^{9/\theta} \text{ l./mole} \\ k_b \sim 10^{13} 10^{-(9+E_a)/\theta} \text{ sec.}^{-1}; k_a \sim 10^{9.8} 10^{-E_a/\theta} \text{ l./mole sec.}$$

Since reaction  $a$  is exothermic,  $E_a \sim 0-7$  kcal./mole. However, reaction 5b of Table IV, Br exchange with *cis*-dibromoethylene, must have a rate constant  $\sim 1/2 k_a$ , and the experimental results fix  $E_a \sim 0$  kcal./mole.

(19) There seems to be some evidence that both of these values may be too high by approximately the same amount.

## Appendix II

Estimation of  $K_{\alpha,\beta}$  and Prediction of  $k_{obsd}$  for Thermal *cis-trans* Isomerization. The double bond strength  $D(\pi)$  in an olefin of the type  $\begin{matrix} R \\ | \\ H > C = C < \\ | \\ H \end{matrix} \begin{matrix} R' \\ | \\ H \end{matrix}$  (*cis* or *trans*) is defined as the heat of the reaction.



Since the heat of formation of the biradical is not readily available, the strength of the double bond can be obtained from the following expression.

$$D_T(\pi) = 2D_T(sec-C-H)^{20} - D_T(H-H) + \Delta H^\circ_{hydrogenation} - \text{resonance energy introduced by R} - \text{resonance energy introduced by R}' \quad (II-2)$$

All the quantities on the right-hand side of eq. II-2 are known or can be estimated for compounds 1, 2, 4, and 5 of Table V at  $\sim 300^\circ\text{K}$ . To correct values to the mean temperatures at which the isomerizations were carried out, the mean value of  $\Delta C^\circ_{p,\beta}$  between that temperature and  $300^\circ\text{K}$ . must be known.

The heat capacity change for any system which changes a double bond for a single bond can be approximated by the  $\Delta C^\circ_p$  for any olefin-alkane pair, these being quite constant, if the "extra" hydrogens on the alkane are taken into account. Such a procedure leads to a value of  $\Delta C^\circ_p = 2.5$  e.u. for such a system at any temperature in the range  $300\text{--}800^\circ\text{K}$ .

$\Delta C^\circ_{p,\alpha,\beta}$  will then depend on the nature of R and R'. If either one introduces a resonance effect, such as benzyl or allylic resonance, the R-C or R'-C bond can be considered as a double bond in the biradical for the purposes of estimating  $\Delta C^\circ_{p,\alpha,\beta}$ . There are then three distinct possibilities:  $\Delta C^\circ_{p,\alpha,\beta} = -2.5, 0,$  or  $+2.5$  e.u. according to whether both R and R' introduce resonance effects, only one does, or neither does.

$\Delta S^\circ_{\alpha,\beta}$  is estimated at  $300^\circ\text{K}$ . as indicated in the text by adding 3 e.u. for each internal rotation gained and subtracting 3 e.u. for each loss of rotation. For electronic degeneracy 2.8 e.u. are added. Temperature corrections are made using appropriate values of  $\Delta C^\circ_{p,\alpha,\beta}$  as described above.

Values of the Arrhenius parameters listed in Table V are obtained as follows.

### (1) *cis*-Butene-2

$$\begin{aligned} D_{300}(\pi) &= 2D(sec-C-H) - D(H-H) + \Delta H^\circ(\text{hydrogenation}) \\ &= 2(94.5)^{21} - 104^{11} - 28.6^{22} = 56.4 \text{ kcal./mole} \\ D_{700}(\pi) &= D_{300}(\pi) + 2.5(0.4) = 57.4 \text{ kcal./mole} \\ E &= 57.4 + 3.5 = 61 \text{ kcal./mole} \end{aligned}$$

(20) If R or R' is a hydrogen atom, primary C-H bond strength should be used.

(21) Assuming the same value as in propane: P. Nangia and S. W. Benson, *J. Am. Chem. Soc.*, **86**, 2773 (1964).

(22) G. W. Wheland, "Resonance in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1955 (no correction has been made for the fact that these values are at  $82^\circ$ ).

$$\Delta S^\circ_{\alpha,\beta}(700^\circ\text{K.}) = 3 + 2.8 + 2.5 \ln(7/3) = 7.9 \text{ e.u.}$$

$$\log A = 11.5 + 1.7 = 13.2$$

### (2) *trans*-Dideuterioethylene

$$\begin{aligned} D_{300}(\pi) &= 2D(\text{primary C-H}) - D(H-H) + \Delta H^\circ(\text{hydrogenation}) \\ &= 2(98)^{12} - 104^{11} - 32.8^{22} = 59.2 \text{ kcal./mole} \end{aligned}$$

$$D_{800}(\pi) = 59.2 + 1.2 = 60.4 \text{ kcal./mole}$$

$$E = 60.4 + 3.5 \sim 64 \text{ kcal./mole}$$

$$\Delta S^\circ_{\alpha,\beta}(800^\circ\text{K.}) = 3 + 2.8 + 2.5 = 8.3 \text{ e.u.}$$

$$\log A = 12.3^{23} + 1.8 = 14.1$$

### (3) *cis*-Stilbene

$$\begin{aligned} D_{300}(\pi) &= 2D(sec-C-H) - 2(\text{benzylic resonance energy}) - D(H-H) + \Delta H^\circ(\text{hydrogenation}) \\ &= 2(94.5)^{21} - 2(14)^{24} - 104^{11} - 26.3^{16} = 30.7 \text{ kcal./mole} \end{aligned}$$

$$D_{800}(\pi) = 30.7 - 2.5(0.3) = 30.0 \text{ kcal./mole}$$

$$E = 30.0 + 3.5 = 33.5 \text{ kcal./mole}$$

$$\Delta S^\circ_{\alpha,\beta}(600^\circ\text{K.}) = -3 + 2.8 - 1.7 = -1.9 \text{ e.u.}$$

$$\log A = 11.3 - 0.4 = 10.9$$

### (4) *cis*-Methyl cinnamate

$$\begin{aligned} D_{300}(\pi) &= 2D(sec-C-H)^{25} - \text{benzylic resonance energy} - \text{carboxylic resonance energy}^{26} - D(H-H) + \Delta H^\circ(\text{hydrogenation}) \\ &= 2(94.5)^{21} - 14^{24} - 4^{26} - 28.7^{22} = 38.3 \text{ kcal./mole} \end{aligned}$$

$$D_{800}(\pi) = 38.3 + 0^{27} = 38.3 \text{ kcal./mole}$$

$$E = 38.3 + 3.5 \sim 42 \text{ kcal./mole}$$

$$\Delta S^\circ_{\alpha,\beta}(600^\circ\text{K.}) = 2.8 \text{ e.u.}$$

$$\log A = 11.3 + 0.6 = 11.9$$

### (5) $\beta$ -Cyanostyrene

Assuming that the  $\text{C}\equiv\text{N}$  group affects  $\Delta H^\circ$  (hydrogenation) the same way as the methyl ester group in (4)<sup>28</sup> and assuming no resonance stabilization of the radical by  $\text{C}\equiv\text{N}$

$$E \sim 46 \text{ kcal./mole}$$

$$\log A = 11.9$$

(23) Rotational rate is higher for ethylene.

(24) S. W. Benson and J. H. Buss, *J. Phys. Chem.*, **61**, 104 (1957).

(25) C-H bond on the  $\alpha$ -carbon may be somewhat weaker.

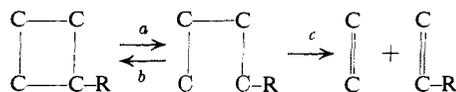
(26) See Appendix III.

(27) Carboxylic resonance energy is small enough so that  $\Delta C^\circ_{p,\alpha,\beta} \sim 0$ .

(28)  $\Delta H$  (polymerization) values differ by  $<2$  kcal./mole.

### Appendix III

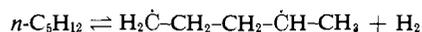
**Carboxylic Resonance Energy.** Carboxylic resonance energy of 4 kcal./mole is deduced from results of Roquette and Walters<sup>29</sup> on the pyrolysis of cyclobutane aldehyde and more recent work (in press) of the same group on the pyrolysis of cyclobutane ethyl ketone. The observed activation energy of  $\sim 54$  kcal./mole for each of the above compounds compares with a value of  $\sim 62$  kcal./mole for the pyrolysis of methylcyclobutane. Assuming the mechanism



$E_{\text{obsd}} = \Delta H_{a,b}^{\circ} + E_c$ . When R is a methyl group,  $\Delta H_{a,b}^{\circ}$  is calculated from the heats of formation of methylcyclobutane and the 1,4-*n*-pentane biradical. The heat of formation of methylcyclobutane is  $\sim -1$

(29) B. C. Roquette and W. D. Walters, *J. Am. Chem. Soc.*, **84**, 4049 (1962).

kcal./mole (estimate based on the affect of methyl group on larger rings) and the heat of formation of the biradical is obtained from considering the following reaction.



$$\begin{aligned} \Delta H_{1,2}^{\circ} &= D(\text{primary C-H}) + D(\text{sec-C-H}) - D(\text{H-H}) \\ &= 98 + 94.5 - 104 = 88.5 \text{ kcal./mole} \\ &= \Delta H_f^{\circ}(\text{biradical}) - \Delta H_f^{\circ}(n\text{-pentane}) \end{aligned}$$

$$\Delta H_f^{\circ}(\text{biradical}) = 88.5 - 35 = 53.5 \text{ kcal./mole}$$

$\Delta H_{a,b}^{\circ} = 54.5$  kcal./mole. If this value is corrected up to the temperature range of the pyrolysis measurements, it will be  $\sim 56$  kcal./mole. This means the activation energy for step *c* is  $\sim 6$  kcal./mole. Assuming that when R is  $-\text{C}(=\text{O})\text{H}$  or  $-\text{C}(=\text{O})\text{R}'$ , the activation energy of step *c* is down to as little as  $\sim 2$  kcal./mole; the value for the over-all activation energy of  $\sim 54$  kcal./mole means that the carbonyl group has at least a  $\sim 4$  kcal./mole resonance energy.

## Catalysis of the *cis* $\rightarrow$ *trans* Isomerization of 2-Hydroxy-5-methylazobenzene

Gunnar Wettermark,<sup>1a</sup> Margaret E. Langmuir,<sup>1b</sup> and Daniel G. Anderson

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The *cis*-*trans* isomerization of 2-hydroxy-5-methylazobenzene in water and ethanol solutions was studied by flash photolysis. In aqueous acetate buffer the thermal *cis*  $\rightarrow$  *trans* conversion of the neutral *cis* molecule HC follows the rate law  $-d[\text{HC}]/dt = (k_S + k_{H^+}[\text{H}^+] + k_{\text{HOAc}}[\text{HOAc}] + k_{\text{OAc}^-}[\text{OAc}^-])[\text{HC}]$ , with  $k_S = 4 \times 10^2 \text{ sec.}^{-1}$ ;  $k_{H^+} = 1.5 \times 10^7$ ,  $k_{\text{HOAc}} = 3.8 \times 10^4$ , and  $k_{\text{OAc}^-} = 6.0 \times 10^3 \text{ l. mole}^{-1} \text{ sec.}^{-1}$  at  $30.0^\circ$ . The mechanism for the proton catalysis proceeds with the *cis*  $\rightarrow$  *trans* conversion of the cation as the rate-determining step; rate constant  $= 2.1 \times 10^4 \text{ sec.}^{-1}$  at  $30.0^\circ$ . The anion in water also undergoes *cis*-*trans* isomerization. Above pH 12, the thermal relaxation of the *cis* anion C<sup>-</sup> follows the rate law  $-d[\text{C}^-]/dt = k_{H^+}'[\text{H}^+][\text{C}^-]$ , with  $k_{H^+}' = 2.0 \times 10^{13} \text{ l. mole}^{-1} \text{ sec.}^{-1}$ . The rate-determining step appears to be the solvent-catalyzed *cis*  $\rightarrow$  *trans* conversion of the neutral species, with rate constant  $= k_S$ . *pK* values of 2.9 and 10.7 were deduced for the *cis* cation and *cis* neutral species, respectively, as compared to  $-1.5$  and  $9.4$  determined for the *trans* species. The same general results for the *cis*  $\rightarrow$  *trans* conversions were obtained in acetate buffered ethanol and sodium ethoxide solutions. An additional, faster transient, probably the hydrazone tautomer, was observed under weakly acidic conditions. Activation energies were estimated for all transformations.

(1) (a) Institute of Physical Chemistry, University of Uppsala, Uppsala, Sweden; (b) please address reprint requests to M. E. L.

### Introduction

The investigation described herein deals with the isomerizations of 2-hydroxy-5-methylazobenzene. Our interest in the isomerizations of a compound having a hydroxyl group *ortho* to the azo bond stemmed from recent investigations in this laboratory of structurally similar anils.<sup>2</sup> It was found that light induces two different isomerizations in *o*-hydroxyanils: (a) *cis*-*trans* about the carbon-nitrogen double bond and (b) a tautomeric hydrogen shift from the hydroxyl group to the nitrogen of the C=N bond. 2-Hydroxy-5-methylazobenzene possesses the possibility of two corresponding isomerizations, *i.e.*, *cis*-*trans* about the N=N bond and azo-hydrazone tautomerism.

Generally the *trans* isomer of an azo compound is the more stable form in solution. The equilibrium may be shifted toward *cis* by photoexcitation and in the dark undergo thermal relaxation to *trans*. This conversion has been shown to be catalyzed by both electrophilic and nucleophilic agents.<sup>3</sup> Only a few systematic studies<sup>3-7</sup> are reported on the catalysis and almost

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