

the result of long term feeding, or tyrosine incorporation may represent only a minor or aberrant biosynthetic pathway. Further data, particularly in regard to the rate of incorporation for individual carbon atoms, are being sought through degradation of thebaine, the primary hydrophenanthrene alkaloid,<sup>5</sup> and should allow proposal of a more definite scheme.

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2-CHLOROCYCLOHEXANONE. ENERGY  
CALCULATIONS FROM INFRARED ABSORPTION  
BANDS BY AREA VS. PEAK-INTENSITY  
MEASUREMENTS

Sir:

As for our estimated value<sup>1</sup> of the energy difference  $\Delta E$  between the e- and the a-isomer of 2-chlorocyclohexanone, Allinger, *et al.*,<sup>2</sup> pointed out that their values were somewhat different from ours, especially for the carbon disulfide solution and they described concentration as a probable cause for the discrepancy. We have now investigated concentration effects and conclude that our data are still valid. The approximation method, using peak intensities, gives incorrect results.

As has been pointed out,<sup>2</sup> infrared evidence does show that the energy difference between the two isomers in a non-polar solution decreases when the dilution proceeds. This behavior may be explained in terms of Onsager's reaction field, because the stable e-isomer is more polar than the other. But it was observed that the intensity ratio ( $C_a A_a / C_e A_e$ ) of the bands assigned to both isomers, respectively, *viz.*, the value of  $\Delta E$ , becomes constant within experimental error, after the dilution proceeds to some extent. The experimental evidence for this is shown in Table I. Area intensities were determined according to the equation  $A = K(1/CL) \ln (T_0/T)_{\nu_{\max}} \times \Delta\nu_{1/2}^a$ , where the letters have their usual meanings. The value of  $K$  was obtained from the table of Ramsay.<sup>3</sup> The suffixes a and e refer to both isomers, respectively. The experimental method was the same as described before.<sup>1</sup>

As can be seen from Table I, the ratio of the observed area intensity of the band at 915  $\text{cm}^{-1}$  to that at 932  $\text{cm}^{-1}$ , *viz.*  $C_a A_a / C_e A_e$ , is 2.6 in the dilute carbon disulfide solution for the concentration range 0.0496 to 0.199 mole/l. This value agrees with that previously reported by us at 0.37 mole/l. and shows the validity of our earlier results.

The value determined in *n*-heptane solution does not differ from the above result within experimental error. The change in the solvent from carbon disulfide to *n*-heptane does not seriously alter the result, since the dielectric constants of both solvents are nearly the same. The data are shown in Table II. As for these cases the results

(1) K. Kozima and Y. Yamanouchi, *J. Am. Chem. Soc.*, **81**, 4159 (1959).

(2) N. L. Allinger, J. Allinger, L. A. Freiberg, R. F. Czaja and N. A. Lebel, *ibid.*, **82**, 5876 (1960).

(3) D. A. Ramsay, *ibid.*, **74**, 72 (1952).

TABLE I  
DEPENDENCE OF THE OBSERVED INTENSITY RATIO ON CON-  
CENTRATION

Temp., 21°; solvent, CS<sub>2</sub>; spectral slit-width,  $S = 2.78$   
 $\text{cm}^{-1}$  at 915  $\text{cm}^{-1}$ ,  $S = 2.87$   $\text{cm}^{-1}$  at 932  $\text{cm}^{-1}$

C (mole/l.)	$\nu_{\max}$	Form	$\ln (T_0/T)_{\nu_{\max}}$	$\Delta\nu_{1/2}^a$	K	$C_a A_a / C_e A_e$
0.794	915	a	0.745	5.2	1.49	2.1
	932	e	.213	8.7	1.51	
.397	915	a	.677	5.4	1.48	2.3
	932	e	.181	8.7	1.51	
.199	915	a	.896	5.4	1.50	2.6
	932	e	.212	8.7	1.51	
.0993	915	a	.970	5.2	1.52	2.6
	932	e	.241	8.1	1.51	
.0496	915	a	1.39	5.4	1.56	2.6
	932	e	.315	9.5	1.53	

TABLE II  
ENERGY DIFFERENCE BETWEEN TWO ISOMERS BY USE OF  
THE BANDS AT 915 AND 932  $\text{CM}^{-1}$

Prism, NaCl; spectral slit-width,  $S = 2.78$   $\text{cm}^{-1}$  at 915  
 $\text{cm}^{-1}$ ,  $S = 2.87$   $\text{cm}^{-1}$  at 932  $\text{cm}^{-1}$ .

Temp	$\nu_{\max}$	Form	$\ln (T_0/T)_{\nu_{\max}}$	$\Delta\nu_{1/2}^a$	K	$C_a A_a / C_e A_e$	Ratio of peak intensities <sup>a</sup>
(1) CS <sub>2</sub> solution (0.37 mole/l.)							
24°	915	a	1.00	4.8	1.53	2.6	4.4
	932	e	0.232	8.0	1.54		
-24°	915	a	1.18	3.7	1.54	2.0	3.5
	932	e	0.346	6.4	1.52		
$\Delta E$ (by area intensity) 0.81 kcal./mole (stable form, e)							
$\Delta E$ (by peak intensity) 0.73 kcal./mole							
(2) <i>n</i> -Heptane solution (0.82 mole/l.)							
56°	915	a	1.30	5.8	1.56	4.5	5.8
	932	e	0.226	7.7	1.49		
7°	915	a	1.62	4.7	1.59	3.5	4.5
	932	e	0.359	6.4	1.48		

$\Delta E$  (by area intensity) 0.92 kcal./mole (stable form, e)  
 $\Delta E$  (by peak intensity) 0.94 kcal./mole

TABLE III  
ENERGY DIFFERENCE BETWEEN TWO ISOMERS BY USE OF  
THE BANDS AT 445 AND 478  $\text{CM}^{-1}$

Prism, KBr; spectral slit-width,  $S = 3.24$   $\text{cm}^{-1}$  at 445  
 $\text{cm}^{-1}$ ,  $S = 3.71$   $\text{cm}^{-1}$  at 478  $\text{cm}^{-1}$ .

Temp.	$\nu_{\max}$	Form	$\ln (T_0/T)_{\nu_{\max}}$	$\Delta\nu_{1/2}^a$	K	$C_a A_a / C_e A_e$	Ratio of peak intensities
(1) CS <sub>2</sub> solution (0.086 mole/l.)							
27°	445	a	0.928	7.4	1.52	0.87	0.83
	478	e	1.12	7.0	1.54		
-20°	445	a	1.40	4.8	1.56	0.71	0.95
	478	e	1.48	6.4	1.56		
$\Delta E$ (by area intensity) 0.64 kcal./mole (stable form, e)							
$\Delta E$ (by peak intensity) -0.40 kcal./mole							
(2) <i>n</i> -Heptane solution (0.097 mole/l.)							
41°	445	a	0.988	10.6	1.55	1.13	0.94
	478	e	1.06	8.8	1.54		
-15°	445	a	1.35	5.9	1.56	0.87	0.96
	478	e	1.40	6.5	1.56		

$\Delta E$  (by area intensity) 0.75 kcal./mole (stable form, e)  
 $\Delta E$  (by peak intensity) -0.10 kcal./mole

did not change significantly even when the peak intensities<sup>2</sup> were used for the evaluation. How-

ever, if, for example, the bands at 445 and at 478  $\text{cm}^{-1}$  were used for the measurements with the KBr optics, the results obtained by use of the peak intensities in the carbon disulfide and the *n*-heptane solution did not agree with the previous one, although results obtained by the area intensities agreed very well. This can be seen from Table III.

Although Allinger, *et al.*, used peak intensities in their estimation of the energy difference, it is not always safe to use peak intensities instead of area intensities. According to our measurements the results obtained by peak intensities cannot be correct, especially when the bands used are lying in the region where the absorption of prisms becomes noticeable. Further evidence for this is given in Table IV.

TABLE IV  
ENERGY DIFFERENCE DETERMINED BY USE OF THE DIFFERENT PRISMS

Temp.	$\nu_{\text{max}}$	Form	$\ln(T_0/T)_{\nu_{\text{max}}}$	$\Delta\nu_{1/2}^a$	$K$	$C_n A_n / C_s A_s$	Ratio of peak intensities
(1) $\text{CS}_2$ solution (0.090 mole/l.); prism, NaCl; spectral slit-width, $S = 2.54 \text{ cm}^{-1}$ at $699 \text{ cm}^{-1}$ , $S = 2.65 \text{ cm}^{-1}$ at $714 \text{ cm}^{-1}$							
22°	699	a	1.36	9.8	1.56	2.6	3.7
	714	e	0.368	14.0	1.55		
-24°	699	a	1.45	8.3	1.56	2.1	3.4
	714	e	0.424	14.0	1.55		
			$\Delta E$ (by area intensity)	0.75 kcal./mole	(stable form, e)		
			$\Delta E$ (by peak intensity)	0.26 kcal./mole			
(2) $\text{CS}_2$ solution (0.090 mole/l.); prism, KBr, spectral slit-width, $S = 2.87 \text{ cm}^{-1}$ at $699 \text{ cm}^{-1}$ ; $S = 2.96 \text{ cm}^{-1}$ at $714 \text{ cm}^{-1}$							
24°	699	a	1.17	9.7	1.56	3.6	3.6
	714	e	0.322	10.0	1.53		
-24°	699	a	1.42	8.9	1.56	2.8	2.8
	714	e	0.507	9.0	1.53		
			$\Delta E$ (by area intensity)	0.78 kcal./mole	(stable form, e)		
			$\Delta E$ (by peak intensity)	0.78 kcal./mole			

It should be noted that the results obtained by area intensities are nearly constant throughout these measurements in good agreement with our previous results.<sup>1</sup>

From the dependence of the intensities on temperature it became clear that both of the bands at 535 and 541  $\text{cm}^{-1}$  are due to the same *e*-isomer. Thus one of the assignments of our previous article should be corrected.

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#### TWO CHEMICAL DETERMINATIONS OF THE POPULATION OF CONFORMATIONS IN 1,3-BUTADIENE

Sir:

For many years it has been generally accepted that at room temperature 1,3-butadiene exists primarily in the *s-trans* form. This contention has been supported by a variety of physical evidence.<sup>1,2</sup>

(1) D. Craig, J. J. Shipman, and R. B. Fowler, *J. Am. Chem. Soc.*, **83**, 2885 (1961).

(2) L. Pauling, "Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 3rd ed., 1960, pp. 290-292.

On the basis of thermodynamic data Aston and Szasz<sup>3</sup> concluded that the *s-cis* form made up 4% of the whole. As late as 1959, Pauling<sup>2</sup> could state that no chemical evidence relating the amounts of the two forms had appeared. We wish now to present such data.

The basis for the determinations reported here is the observation by Walling, *et al.*,<sup>4</sup> that the free radical chlorination of *cis* or *trans* 2-butene produced only the respective *cis*- or *trans*-1-chloro-2-butenes. This result was interpreted as meaning that the short-lived allylic free radicals, produced during the chlorination reaction, were capable of maintaining their original geometry. If this is so, then it is evident that an examination of the 1,4-addition products formed by radical attack on butadiene may offer a direct measurement of the amounts of *s-trans*- and *s-cis*-butadiene present in the reaction mixture. It should be pointed out, however, that in the slower chain propagating step of the radical polymerization of butadiene the ratio of *cis* to *trans* double bonds in the product varies considerably with temperature.<sup>5</sup> Thus, the use of this method for determining the population of conformations in 1,3-butadiene will be most reliable in cases where the life time of any intermediate allylic radicals is comparatively short.

The electrolysis of potassium acetate in methanol-butadiene mixtures has been shown previously to lead to 3-methyl-1-pentene and *trans*-3-hexene among other products.<sup>6</sup> In the original studies no *cis*-3-hexene was observed and an argument was advanced postulating a heterogeneous reaction involving absorbed radicals. We now find that by using a fifty-foot column of 23% dimethylsulfolane on Chromosorb at room temperature it is possible to demonstrate the presence of *cis*-3-hexene in the reaction product by vapor phase chromatography. The hexene fraction from the Kolbe electrolysis gave the analysis: 3-methyl-1-pentene, 21% *trans*-3-hexene, 77%; and *cis*-3-hexene, 2%. Their results indicate that *ca.* 97% of the butadiene exists in the *s-trans* form while *ca.* 3% is in the *s-cis* form. The close agreement between the experimental observation and the predicted values<sup>3</sup> suggests strongly that no special effects need be evoked to explain the products from the Kolbe electrolysis, and that we are actually measuring the population of butadiene conformers.

Kharasch, Holton, and Nudenberg<sup>7</sup> have reported that the treatment of methyl iodide with magnesium in the presence of isoprene does not yield any 1,2- or 1,4-addition products of methyl radicals to the isoprene in contrast to the results with other alkyl halides. However, we find that when methyl iodide and magnesium react in the presence of butadiene a small yield of hexenes is formed. The analysis of this mixture gave the results: 3-methyl-1-pentene, 26%; *trans*-3-hexene,

(3) J. G. Aston and G. Szasz, *J. Chem. Phys.*, **14**, 67 (1946).

(4) C. Walling, B. B. Jacknow, and W. Thaler, Abstracts, 136th National Meeting, American Chemical Society, Atlantic City, N. J.

(5) C. Walling, "Free Radicals in Solution," John Wiley and Sons, New York, N. Y., 1957, p. 230.

(6) W. B. Smith and H.-G. Gilde, *J. Am. Chem. Soc.*, **81**, 5325 (1959), and **83**, 1355 (1961).

(7) M. S. Kharasch, P. G. Holton, and W. Nudenberg, *J. Org. Chem.*, **19**, 1600 (1954).