

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MISSISSIPPI, UNIVERSITY, MISS.]

Mechanism of the Pyrolysis of Bicyclo[2.2.1]heptadiene. Kinetics of the Bicyclo[2.2.1]heptadiene to Toluene Isomerization

BY WILLIAM C. HERNDON AND LYLE L. LOWRY¹

RECEIVED OCTOBER 23, 1963

Four concurrent and consecutive first-order reactions occur during the thermal decomposition of bicyclo[2.2.1]heptadiene. The rate constants for all four of these reactions have been determined over the temperature range 344 to 431° in a gas phase stirred flow reactor. The Arrhenius equation for the previously unreported bicycloheptadiene to toluene conversion is $k = 10^{14.23} \exp(-53,140/RT)$ sec.⁻¹. A common intermediate is suggested for only two of the three isomerizations which occur in this system.

A remarkable number of thermal decompositions and isomerizations center around the bicyclo[2.2.1]heptadiene-, cycloheptatriene-, toluene system. Bicycloheptadiene undergoes a reverse Diels-Alder reaction to yield cyclopentadiene and acetylene and simultaneously undergoes isomerization to cycloheptatriene and toluene.^{2,3} Bicyclo[3.2.0]hepta-2,6-diene gives cycloheptatriene and possibly toluene upon pyrolysis,^{4,5} and bicyclo[4.1.0]heptadiene (norcadiene) is presumably thermally unstable with respect to cycloheptatriene.⁶ The mass spectrum of spiro[2.4]hepta-1,3-diene is virtually identical with those of cycloheptatriene and toluene⁷ which suggests that it may thermally decompose to give cycloheptatriene and/or toluene. In addition to the foregoing reactions, cycloheptatriene also undergoes rapid conversion of the 7- and 3-positions as evidenced by the low temperature (100–140°) isomerization of 7-deuteriocycloheptatriene.⁸

The kinetics of the bicyclo[2.2.1]heptadiene decomposition to give cyclopentadiene and acetylene and the concurrent isomerization to yield cycloheptatriene have been determined by Birely and Chesick.⁹ Fortunately toluene was formed in quite small amounts and could be included with the cycloheptatriene. With this simplification the system becomes that of two concurrent first-order reactions easily solved by conventional methods. The reactions were homogeneous, and the rate constants in the Arrhenius form are k_1 (subscripts refer to eq. 1) = $5.2 \times 10^{14} \exp(-50.5 \pm 1.2 \text{ kcal./RT}) \text{ sec.}^{-1}$ and $k_2 = 8.2 \times 10^{14} \exp(-51.6 \pm 1.8 \text{ kcal./RT}) \text{ sec.}^{-1}$.

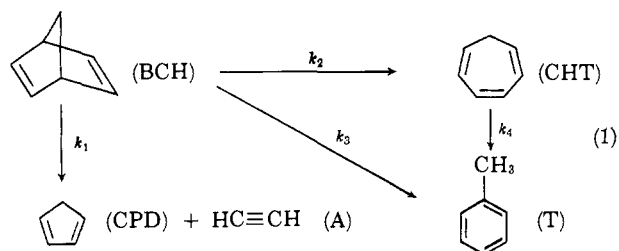
Later Klump and Chesick¹⁰ studied the cycloheptatriene to toluene conversion independently. The rate constant for this reaction was $k_4 = 3.5 \times 10^{13} \exp(-51.1 \pm 0.8 \text{ kcal./RT}) \text{ sec.}^{-1}$. A comparison of the conversion to toluene at 370° in this reaction with the yield of toluene in the previous reaction at the same temperature made it appear likely that some toluene is

formed directly from bicycloheptadiene as well as from cycloheptatriene. However, a referee quoted by Meyerson, McCollum, and Rylander¹¹ is said to have shown "that the thermal isomerization of bicycloheptadiene proceeds first to cycloheptatriene and then to toluene, and that the two products are not formed from a common intermediate."

We considered that a common intermediate was a likely possibility during the formation of cycloheptatriene and toluene, and so we decided to see if we could definitely prove that some toluene was produced from bicycloheptadiene without the intervention of cycloheptatriene and if the Arrhenius parameters for such a reaction might help in defining its nature.

Kinetic Method

To show that toluene is formed simultaneously from bicycloheptadiene and cycloheptatriene and determining the rate constants would be prohibitively difficult by conventional kinetic methods. The system is one involving three concurrent and one consecutive first-order reactions as shown in eq. 1. Exact integrated rate expressions can be derived for the variation of concentration with time for each



moiety, and these equations could be utilized in a manner analogous to that of Swain,¹² or the system could be treated by the general computer method devised by de Maine.¹³ However, we decided to use a gas phase stirred flow reactor similar to that introduced by Lewis and Herndon.¹⁴ This flow reactor is so constructed that the contents of the reactor are completely mixed by diffusion thereby leading to uniform concentrations which become time-invariant within the reactor. Such a system allows one to calculate the rate constants for any number of concurrent and consecutive reactions from simple algebraic equations rather than differential or integrated rate expressions.

(1) This work was supported by Grant No. GP247 from the National Science Foundation. L. L. Lowry was a participant in the University of Mississippi National Science Foundation Summer Research Program for High School Teachers (1963).

(2) W. G. Woods, *J. Org. Chem.*, **23**, 110 (1958).

(3) W. M. Halper, G. Gaertner, E. W. Swift, and G. E. Pollard, *Ind. Eng. Chem.*, **50**, 1131 (1958).

(4) W. G. Dauben and R. L. Cargill, *Tetrahedron*, **12**, 186 (1961).

(5) M. V. Evans and R. C. Lord, *J. Am. Chem. Soc.*, **83**, 3409 (1961).

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(7) S. Meyerson and P. N. Rylander, *J. Chem. Phys.*, **27**, 901 (1957).

(8) A. P. ter Borg, H. Kloosterziel, and N. van Meurs, *Proc. Chem. Soc.*, 359 (1962). However, see also A. G. Harrison, L. R. Honnen, H. J. Dauben, Jr., and F. P. Lossing, *J. Am. Chem. Soc.*, **82**, 5593 (1960), who obtained only ethylbenzene, no xylene, from thermal decomposition of 7-methylcycloheptatriene, and W. von E. Doering and P. P. Gaspar, *ibid.*, **85**, 3043 (1963), who found that cycloheptatriene-7,7-*d*₂ did not exchange at 97°.

(9) J. H. Birely and J. P. Chesick, *J. Phys. Chem.*, **66**, 568 (1962).

(10) K. N. Klump and J. P. Chesick, *J. Am. Chem. Soc.*, **85**, 130 (1963).

(11) S. Meyerson, J. D. McCollum, and P. N. Rylander, *ibid.*, **83**, 1401 (1961), footnote 23.

(12) C. G. Swain, *ibid.*, **66**, 1696 (1944).

(13) P. A. D. de Maine, "Digital Computer Programs for Physical Chemistry," Vol. 11, The Macmillan Co., New York, N. Y., in press.

(14) E. S. Lewis and W. C. Herndon, *J. Am. Chem. Soc.*, **83**, 1955 (1961).

Denbigh,¹⁵ Burnett and Hammett,¹⁶ and Lee, Smid, and Szwarc¹⁷ have previously presented equations for complex reactions in liquid phase stirred flow reactors, but systems similar to the one investigated herein have not been described.

If the reactions shown in eq. 1 take place in a stirred flow reactor, then the expressions which interrelate the volume of the reactor V , the flow rate of the exit gas U (reactants, products, and inert carrier gas), the first-order rate constants for the various reactions k_i , and the concentrations of each product and reactant in the reactor are

$$k_1 V(\text{BCH}) = U(\text{CPD}) \quad (2)$$

$$k_2 V(\text{BCH}) = U(\text{CHT}) + k_4 V(\text{CHT}) \quad (3)$$

$$k_3 V(\text{BCH}) + k_4 V(\text{CHT}) = U(\text{T}) \quad (4)$$

Equations 2, 3, and 4 simply express the fact that at a steady state in a stirred flow reactor the rate of appearance of any component is equal to its rate of disappearance.

These equations can be rearranged to give

$$U/V = k_1(\text{BCH})/(\text{CPD}) \quad (5)$$

$$U/V = k_2(\text{BCH})/(\text{CHT}) - k_4 \quad (6)$$

$$U/V \times (\text{T})/(\text{CHT}) = k_3(\text{BCH})/(\text{CHT}) + k_4 \quad (7)$$

With analyses of the contents of the reactor at various flow rates, the rate constants can be determined from the slopes and intercepts of straight lines as shown in eq. 5, 6, and 7. If toluene is formed only from bicycloheptadiene, eq. 7 will have a zero intercept. If toluene is formed solely from cycloheptatriene, eq. 7 will give a straight line with a zero slope.

Experimental

Apparatus and Method.—In the flow system, which was constructed from Pyrex glass, a stream of dried prepurified nitrogen gas controlled by a needle valve flowed into a vaporizer containing bicyclo[2.2.1]heptadiene. The gas stream, which now contained bicycloheptadiene vapor, then passed into the reactor and finally through a soap-bubble flow meter. The vaporizer was maintained at room temperature for most of the experiments but was cooled to 0° in some experiments in order to vary the partial pressure of reactant in the gas phase.

The reactor was spherical, had a volume of 52.4 ml., and was assumed to be well stirred by diffusion, an assumption previously shown to be sufficiently good for kinetic purposes.¹⁸ It was immersed in a molten lead constant temperature bath and heated electrically, the majority of the heat being supplied from a Sola constant voltage transformer and a Powerstat, and the controlling heat supplied by a Bailey proportional controller. The temperatures of the bath and of the reacting gas were measured by Chromel-Alumel thermocouples calibrated against a platinum resistance thermometer. Temperature control was better than $\pm 0.1^\circ$, and the absolute temperature is known to better than 0.6°.

The flow rate of the exit gas was measured by timing the rise of a soap bubble in a 25-ml. buret with an electric timer. The gas stream was sampled just before it entered the reactor and just after it left the reactor through serum bottle stoppers inserted in the line. The gas samples were withdrawn with a 1-ml. hypodermic syringe and analyzed by gas chromatography, utilizing a Wilkens Instrument Co. Aerograph Model A-90-P thermal conductivity gas chromatograph. At 100° all of the

reactants and products except acetylene were separable with a 20%, 5-ft., GE SF-96 silicone column. Three to five samples were obtained at each flow rate, and integrated areas were used to calculate relative concentrations. Known mixtures were used to calibrate the nonlinear response of the detector. The products and reactant were identified by comparisons of retention times and infrared spectra with those of the known compounds.

The possible random and systematic errors inherent in this method have been discussed previously,¹⁸ and the resultant error in a calculated rate constant is estimated to be approximately $\pm 2.5\%$.

Chemicals.—Bicyclo[2.2.1]heptadiene was obtained from Matheson Co., Inc., and from the Aldrich Chemical Co. Very small amounts of impurities were removed by bubbling nitrogen through the liquid bicycloheptadiene for a few hours. Cyclopentadiene was obtained by cracking dicyclopentadiene from K and K Laboratories, Inc. The cycloheptatriene was a product of the Fisher Scientific Co. and contained 0.7% toluene.

Results

The thermal decomposition of bicyclo[2.2.1]heptadiene was studied in a gas phase stirred flow reactor at seven different temperatures over the range 344 to 431°. Table I contains the data for pyrolysis at 400.6° and the results presented therein are typical.

TABLE I
PYROLYSIS AT 400.6°

U/V , l./sec. $\times 10^2$	(BCH/CPD)	(BCH/CHT)	(T)/(CHT)
1.475	0.635	0.894	0.135
1.230	.534	.745	.150
0.654	.278	.418	.226
.453	.199	.300	.297
.281	.123	.211	.459
.137	.056	.107	.852

Figures 1, 2, and 3 are graphical presentations of eq. 5, 6, and 7, respectively, for the data in Table I. Equation 7 (Fig. 3) has a nonzero intercept and slope consistent with the postulated formation of toluene by two different first-order routes.

Table II presents the rate constant at the different temperatures. At each temperature three to five gas

TABLE II

RATE CONSTANTS (SEC.⁻¹) FOR BICYCLOHEPTADIENE PYROLYSIS

Temp., °C.	k_1 (BCH → CPD)	k_2 (BCH → CHT)	k_3 (BCH → T)	k_4 (CHT → T)
343.8	6.50×10^{-4}	4.65×10^{-4}	2.42×10^{-5}	2.63×10^{-5}
357.5	1.75×10^{-3}	1.26×10^{-3}	6.81×10^{-5}	7.16×10^{-5}
375.8	5.81×10^{-3}	4.16×10^{-3}	2.41×10^{-4}	2.55×10^{-4}
389.1	1.15×10^{-2}	7.92×10^{-3}	4.93×10^{-4}	4.96×10^{-4}
400.6	2.31×10^{-2}	1.73×10^{-2}	1.04×10^{-3}	1.05×10^{-3}
416.3	5.31×10^{-2}	3.86×10^{-2}	2.52×10^{-3}	2.54×10^{-3}
430.8	1.03×10^{-1}	7.72×10^{-2}	5.16×10^{-3}	4.98×10^{-3}

samples were analyzed for each of six different flow rates. Then the rate constants were determined from the slopes and intercepts of straight lines analogous to those in Fig. 1, 2, and 3 by the method of least squares. An IBM 1620 computer was used to process the data. The standard deviations of the rate constants center around 2% with later experiments much more precise, and a redetermination of the values for the rate constants at 389° after a lapse of 2 months gave values within 3% of the former values. A comparison of the rate constants determined in this work with those predicted by the Arrhenius equations of Birely and Chesick⁹ and Klump and Chesick¹⁰ gives very close agreement. The Arrhenius parameters found in this work with their standard deviations are given in Table III.

(15) K. G. Denbigh, *Trans. Faraday Soc.*, **43**, 648 (1947).

(16) R. L. Burnett and L. P. Hammett, *J. Am. Chem. Soc.*, **80**, 2415 (1958).

(17) C. L. Lee, J. Smid, and M. Szwarc, *ibid.*, **85**, 912 (1963).

(18) W. C. Herndon, M. B. Henly, and J. M. Sullivan, *J. Phys. Chem.*, **67**, 2843 (1963).

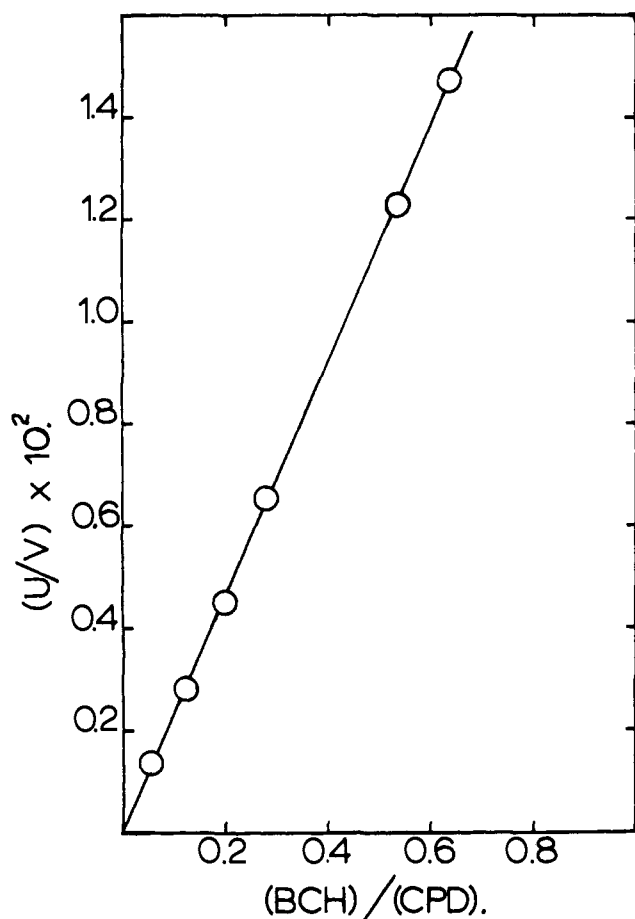


Fig. 1.—Plot of eq. 5. The slope is the rate constant for formation of cyclopentadiene from bicycloheptadiene at 400.6°.

Since the rate constants for these simultaneous reactions were determined under identical conditions, one might expect that the differences in activation energies and pre-exponential factors which can be estimated from the relative rates at the various temperatures would be known with higher precision than the actual Arrhenius parameters. Various rearrangements and

TABLE III
ARRHENIUS PARAMETERS

Reaction	log A	E_a , cal./mole
BCH \rightarrow CPD + A	14.62 \pm 0.25	50,190 \pm 760
BCH \rightarrow CHT	14.68 \pm .26	50,610 \pm 780
BCH \rightarrow T	14.23 \pm .24	53,140 \pm 730
CHT \rightarrow T	13.90 \pm .28	52,100 \pm 820

combinations of eq. 5, 6, and 7 can be made to give the relative rate constants which yield the relative activation parameters shown in Table IV. Bicycloheptadiene isomerization to cycloheptatriene was chosen as the

TABLE IV
RELATIVE ACTIVATION PARAMETERS

Reaction	ΔE_a	$\Delta \log A$
BCH \rightarrow CPD	-420 \pm 280	-0.002 \pm 0.09
BCH \rightarrow CHT
BCH \rightarrow T	+2530 \pm 230	+0.39 \pm 0.07
CHT \rightarrow T	+1490 \pm 250	+0.72 \pm 0.08

reference reaction and the differences in activation energies were estimated by the method of least squares using the Arrhenius equation. The standard deviations of these differences are seen to be quite small.

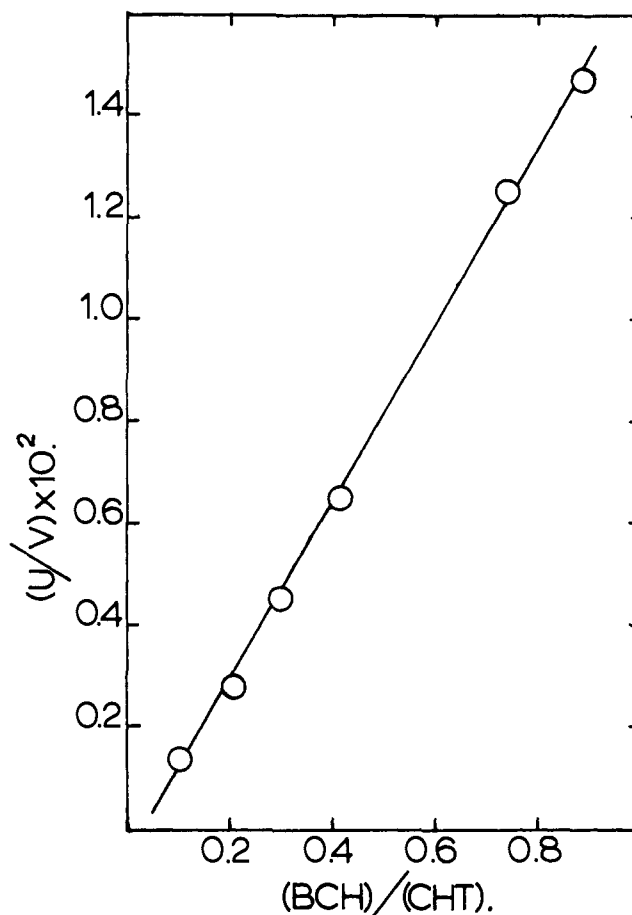
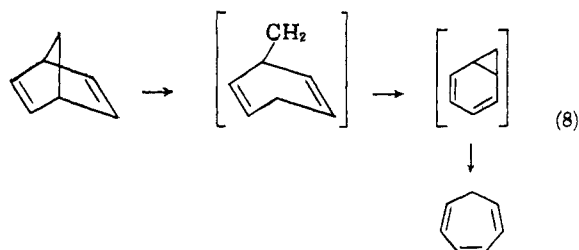


Fig. 2.—Plot of eq. 6. The slope is the rate constant for formation of cycloheptatriene from bicycloheptadiene at 400.6°.

Discussion

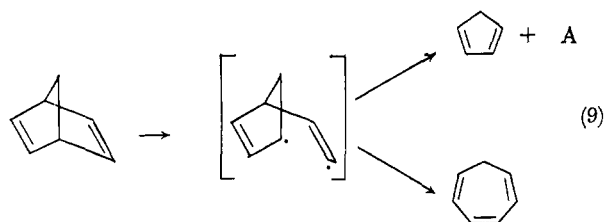
The close correspondence of these reactions to the kinetic equations developed here is evidence that all of the reactions are first order and presumably unimolecular. The activation parameters for the three previously investigated reactions^{9,10} are in very good agreement even though our results cover a much larger temperature range. The previously undetermined Arrhenius energy of activation for the bicycloheptadiene to toluene isomerization seems reasonable, and the pre-exponential factor is of the normal magnitude for unimolecular isomerizations.

A number of mechanistic possibilities have been suggested for the pyrolysis of bicyclo[2.2.1]heptadiene. For the reaction bicycloheptadiene to cycloheptatriene, Woods² proposed a diradical obtained from homolytic cleavage of the C₇-C₁ bond and norcaradiene as transient intermediates.



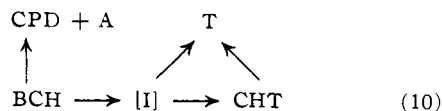
Birely and Chesick⁹ have proposed a common diradical intermediate, formed by rupture of a bridgehead carbon-vinyl carbon bond, for both the reverse Diels-

Alder reaction and the isomerization to cycloheptatriene. They also mention a possible bicyclo[3.2.0]-heptadiene intermediate.

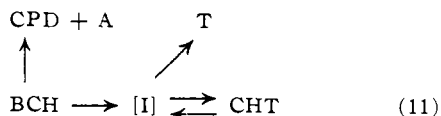


Since it has now been shown that toluene is formed without the intervention of cycloheptatriene concurrently with toluene from cycloheptatriene, three more possibilities for the over-all mechanism can be suggested. It is possible that each reaction is separate and distinct, and this is the gross mechanism pictured in eq. 1.

Another possibility involves a reverse Diels-Alder reaction to give cyclopentadiene and acetylene, concurrent formation of a common intermediate which rearranges to cycloheptatriene and toluene, and a consecutive reaction of cycloheptatriene to yield toluene as indicated in eq. 10.



Finally the mechanism in eq. 11 entertains the possibility of a common intermediate for all of the isomerizing reactions and a concurrent decomposition to acetylene and cyclopentadiene.



The nature or existence of the proposed intermediates cannot be deduced by kinetic analysis at a single temperature. If the intermediates are highly reactive, each mechanism yields algebraic equations of precisely the same form as eq. 2, 3, and 4. However, the relative activation parameters obtained for the four reactions in this work do allow one to exclude two of the possibilities.

Birely and Chesick⁹ propose that the similarity of activation parameters for the decomposition to cyclopentadiene and the isomerization to cycloheptatriene is evidence for a common initial step as shown in eq. 9. A least squares analysis of their reported rate data gives results which are even more similar with $\log k_1 = (13.64 \pm 0.15) - (50,430 \pm 370/2.3RT)$ and $\log k_2 = (13.44 \pm 0.32) - (50,426 \pm 1234/2.3RT)$. The indicated error limits are standard deviations and, as one can see, the results are in very precise agreement with our results as reported in Tables III and IV. *Even so, we consider the similar activation parameters to be evidence against the formation of a common intermediate and to be evidence only for similar initial steps.*

If a common intermediate for the reverse Diels-Alder reaction and the isomerization to cycloheptatriene did exist, then the ratio of the rate constants, as measured by us or by Birely and Chesick, can be shown to be the ratio for the reactions which occur after the common intermediate is formed. An Arrhenius plot of this ratio

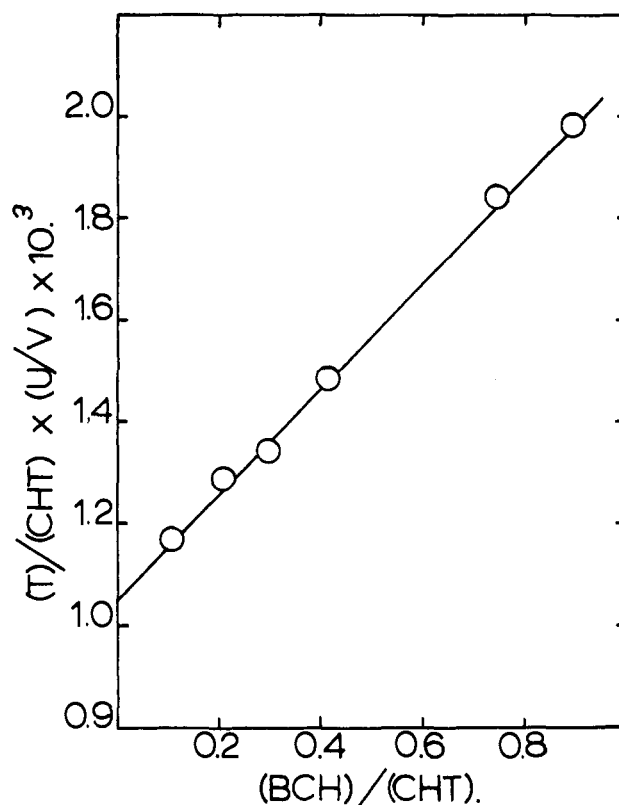


Fig. 3.—Plot of eq. 7. The slope is the rate constant for formation of toluene from bicycloheptadiene and the intercept is the rate constant for formation of toluene from cycloheptatriene at 400.6°.

gives the difference in activation energies and the ratio of the pre-exponential factors for the two subsequent reactions. This difference is only 400 cal. from our work and 0 cal. from the corrected values of Birely and Chesick, and the pre-exponential A factors are essentially the same. This indicates that the two processes occurring after the common intermediate are essentially similar. Since we know they are not (one involves simply breaking a second vinyl carbon-bridgehead carbon bond, but the other must involve rotation of the vinyl radical with attack on the 7-carbon to form a bond), then a common intermediate for these two reactions must not exist. So the similarity of activation parameters in these reactions is not evidence for a common intermediate.¹⁹

Our supposition of a common intermediate for all of the isomerization reactions, mechanism 11, can also be shown to be incorrect. If it were correct, then the ratio of the rate constant for formation of intermediate from bicycloheptadiene to the rate constant for formation of intermediate from cycloheptatriene can be found as the intercept of the line obtained when $[(\text{T}) + (\text{C} \text{HT})]/(\text{BCH})$ is plotted *vs.* $(\text{T})/(\text{C} \text{HT})$. A plot of this ratio of rate constants *vs.* $1/T$ should give the difference in activation energies for formation of the common intermediate from bicycloheptadiene and cycloheptatriene. This difference obtained from such a plot is $+4.3 \pm 0.4$

(19) A referee has pointed out that if the Birely and Chesick scheme were correct and the common intermediate were a step in a retro-Diels-Alder reaction, one should anticipate the formation of cycloheptatriene during the Diels-Alder synthesis of bicycloheptadiene. A search of the literature reveals no information on this subject; however, the condensation of cyclopentadiene with acetylene in this laboratory at 200 lb. pressure and 180° gave bicycloheptadiene in 20% yield and no cycloheptatriene could be detected by gas chromatography.

kcal./mole. This difference in activation energies should also be very close to the difference in heats of formation or combustion of bicycloheptadiene and cycloheptatriene. Of course, the preceding argument is based on the assumption that the two transition states closely resemble the reactive intermediate.²⁰ The energy difference $\Delta\Delta H_f^\circ$ at 25° calculated from the heats of formations of gaseous bicycloheptadiene^{21,22} and cycloheptatriene²³ is $+13.6 \pm 0.5$ kcal./mole, and this difference should be approximately the same at higher temperatures. The nonconcurrency of the experimental and theoretical energy difference strongly indicates that the assumption is incorrect and that there is not a common intermediate to the three isomerizations.

With the present state of knowledge, one cannot distinguish between the further possibilities, four distinct

(20) G. S. Hammond, *J. Am. Chem. Soc.*, **77**, 334 (1955).

(21) A. F. Bedford, A. E. Beezer, C. T. Mortimer, and H. D. Springall, *J. Chem. Soc.*, 3823 (1963).

(22) C. T. Mortimer, "Reaction Heats and Bond Strengths," Pergamon Press, New York, N. Y., 1962, p. 44.

(23) H. L. Finke, D. W. Scott, M. E. Gross, J. F. Messerly, and G. Waddington, *J. Am. Chem. Soc.*, **78**, 5469 (1956).

reactions (eq. 1) or the mechanism shown in eq. 10. However, we do consider the latter to be the more likely with a diradical intermediate obtained from cleavage of a C₇-C₁ bond. It is hard to imagine two dissimilar initial steps leading from bicycloheptadiene to cycloheptatriene and toluene. Also, as Klump and Chesick¹⁰ have pointed out, a state quite similar to norcaradiene is required for the cycloheptatriene to toluene isomerization. Since we have shown that this reaction and the isomerizations of bicycloheptadiene to cycloheptatriene and toluene must be considered separately, such a norcaradiene state is not possible for the bicycloheptadiene isomerizations.

Kinetic experiments with substituted bicycloheptadienes and cycloheptatrienes are presently being carried out in an effort to define more closely the natures of these reactions.

Acknowledgments.—The financial support of the National Science Foundation is deeply appreciated. We also wish to thank Richard D. Ross of the University of Mississippi Computer Center for his kind assistance.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF TEXAS, AUSTIN, TEXAS]

The Electrochemistry of Diphenylpicrylhydrazyl¹

BY EMANUEL SOLON AND ALLEN J. BARD²

RECEIVED NOVEMBER 30, 1963

The electroreduction and oxidation of diphenylpicrylhydrazyl (DPPH), a stable free radical, at a platinum electrode in acetonitrile solutions was investigated using voltammetry, chronopotentiometry, and controlled potential coulometry. The results showed that DPPH is reduced and oxidized in reversible, one-electron reactions. A brief study of the electrode reactions in methanol, ethanol, acetone, and dimethyl sulfoxide was also made.

Diphenylpicrylhydrazyl (DPPH, I), a stable free radical first prepared by Goldschmidt and Renn,³ has been of interest as a standard in electron spin reso-



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nance (e.s.r.) spectroscopy and as a free radical scavenger and counter. The electrode reactions of DPPH are of interest because free radicals are frequently intermediates and products of electrode reactions; the electro-generated radicals usually then react with the solvent, couple, or undergo further electrode reactions. A study of the electrochemistry of DPPH was undertaken to investigate the characteristics of electrode reactions of free radicals, to study the possibility of employing DPPH as a radical scavenger during electrode reactions, and to evaluate electroanalytical methods for the determination of DPPH. The electroreduction and oxidation of DPPH at a platinum electrode in acetonitrile

solutions was investigated using voltammetry, chronopotentiometry, and controlled potential coulometry. A brief study of the electrode reactions of DPPH in some other solvents was also undertaken.

Results and Discussion

Voltammetry.—A typical current-potential curve for the voltammetric oxidation and reduction of DPPH at a rotating platinum electrode (r.p.e.) in an acetonitrile solution containing 0.1 M NaClO₄ is shown in Fig. 1. The curves showed a single cathodic wave and a single anodic wave of equal height; the half-wave potentials ($E_{1/2}$) of both waves were independent of concentration of DPPH or NaClO₄ (Table I). Plots of potential *vs.* $\log [i_{lim}/(i_{lim}-i)]$, with potentials corrected for iR drop, were linear, with slopes of about 0.06 for both waves. The reversibility of both waves was shown by current-potential curves taken with solutions containing mixtures of DPPH and its oxidation product (R⁺) or its reduction product (R⁻) (obtained by controlled potential electrolysis of DPPH solutions at the limiting current plateau of the waves). For both mixtures of DPPH and R⁻ and DPPH and R⁺ the current-potential curves were only shifted vertically, along the current axis; $E_{1/2}$'s remained constant and the curves passed through the zero current axis without inflection. The waves correspond therefore to the following re-

(1) (a) Based on a thesis submitted by E. Solon in partial fulfillment of the requirements for the degree of Ph.D., August, 1963. (b) Presented at the 145th National Meeting of the American Chemical Society, New York, N. Y., September, 1963.

(2) To whom correspondence and request for reprints should be directed.

(3) S. Goldschmidt and K. Renn, *Ber.*, **56**, 628 (1922).