

acetylene. The efficiency of oxygen as a free radical scavenger is well known¹⁶ and it is probably this property that resulted in the inhibition of the acetylene-forming reaction. Other investigators have detected free radicals as intermediates in chemical conversions brought about by ultrasonic waves.²

The appearance of carbon dioxide in significant amounts in the reaction products when the reaction is carried out in an atmosphere of oxygen is consistent

(16) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, Chap. 9.

with the assumption that oxygen is serving as a radical scavenger. It is of interest that the percentage of C-atoms recovered as acetylene in the presence of argon approximates that recovered as carbon dioxide in the presence of oxygen.

Since the experiments run in an oxygen atmosphere were conducted in the presence of silver nitrate and the acetylene precipitated as silver acetylide, the question arose whether silver acetylide was reacting with oxygen to produce carbon dioxide. Control experiments proved that such was not the case.

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The Thermal Isomerization of Tropilidene

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The thermal isomerization of tropilidene to toluene has been observed in the gas phase in the temperature range 363–408°, and in the pressure range 0.9–19.7 mm. The first-order rate constant was found to be independent of the surface to volume ratio, and unchanged both by nitric oxide addition and by a 20-fold increase in pressure through nitrogen addition. The rate constant for the reaction is given by $k = 3.5 \times 10^{13} \exp[(-51.1 \pm 0.8) \text{ kcal./RT}] \text{ sec.}^{-1}$. The activation energy precludes a simple carbon-carbon bond rupture as the initial step, and a species at least formally similar to norcaradiene is suggested as the reactive intermediate.

Introduction

The structure of tropilidene has been the subject of a wide variety of physical and chemical investigations. Physical chemical studies indicate that the principal species is 1,3,5-cycloheptatriene, whereas many chemical reactions suggest that norcaradiene, or (0,1,4)bicyclohepta-2,4-diene, is the principal species. For example, Lord and Evans² state that the infrared and Raman absorptions between 2850 and 2967, cm.^{-1} preclude norcaradiene since this bicyclic compound would be expected to possess only vinyl and cyclopropyl carbon-hydrogen stretching frequencies which would be no lower in frequency than 2970 cm.^{-1} . The n.m.r. spectrum exhibiting six vinyl and two aliphatic protons is also incompatible with the norcaradiene formulation.³

Recent X-ray single crystal structure analyses of the *p*-bromophenacyl ester of thujic acid shows a non-planar cycloheptatriene ring with alternating single and double bonds.⁴

However the reaction of tropilidene with maleic anhydride yields products formally derived from norcaradiene. That is, they are tricyclic products containing a cyclopropane ring, rather than the bicyclo-(3,2,2)nona-2,6-diene system expected from a reaction with 1,3,5-cycloheptatriene.⁵ On quantitative ozonolysis 7-tropilidenecarboxylic acid takes up only two moles of ozone, a reaction more characteristic of norcaradiene than of cycloheptatriene.⁶

Other oxidizing agents produce *cis*-1,2-cyclopropanedicarboxylic acids.⁷

The pyrolysis of tropilidene to toluene was observed by Woods,⁸ and 7-methyltropilidene has been pyrolyzed to yield ethylbenzene.⁹ This reaction could take place either by means of radical chain processes which would involve species such as benzyl radicals as intermediates, or by means of a unimolecular reaction

path. One such unimolecular reaction mechanism to be considered would be a process analogous to the cyclopropane isomerization to propylene involving a small amount of norcaradiene in rapid equilibrium with cycloheptatriene. Hence, a kinetic study of this reaction was undertaken in the hopes that the nature of the reaction, radical or unimolecular, could be demonstrated. Knowledge of the Arrhenius factors for a unimolecular process might also then be of value in considering the details of this rearrangement.

Experimental

The tropilidene used in this work was Shell Chemical material which was first separated from polymer and oxygenated species by a simple vacuum distillation. The resulting material, yellow in color and containing about 10% of toluene, was then finally purified for use in 0.15-ml. batches by means of gas chromatography. A 12 m., 0.25-in. o.d. column packed with Dow-Corning 710 silicone oil on 45-60 mesh Gas Chrom-CI support was used at 100° for both the starting material preparation and run product analysis. The cycloheptatriene from the g.l.p.c. purifications was colorless and contained from 1.5% to 0.1% of toluene as an impurity. The appropriate corrections for this toluene and the reaction vessel inlet dead volume were made in calculations of rate constants. The cycloheptatriene and toluene peaks were quite well resolved and symmetrically shaped when the samples of products from the kinetic runs were run through the column. The starting material was degassed on the vacuum line at liquid nitrogen temperature before use. Matheson prepurified nitrogen and nitric oxide were used without further treatment in the runs with cycloheptatriene mixtures.

The vacuum line and air-bath thermostat with 500-ml. reaction vessel were used essentially as described previously.¹⁰ Temperature measurements were also performed as previously described using thermocouples and a standard platinum resistance thermometer. Temperatures were generally constant to $\pm 0.1^\circ$ during the course of each run, and the precision of absolute temperature measurement should be comparable. Temperature accuracy is probably $\pm 0.4^\circ$.

The purified cycloheptatriene was stored at Dry Ice temperature until needed. The desired pressure of reactant was admitted to the manifold and expanded into the reaction vessel to start the run.

Products were frozen in a liquid nitrogen cooled trap immediately after passage from the reaction vessel through the mercury float valve. The trap contents were then frozen into a detachable sample tube. About 20 microliters of pentane was added to the small volume of cold products in the sample tube as a carrier. The whole mixture was then syringe injected into the heated inlet of the gas chromatograph. Peak area measure-

(1) Department of Chemistry, Haverford College, Haverford, Pa.

(2) M. V. Evans and R. C. Lord, *J. Am. Chem. Soc.*, **82**, 1876 (1961).

(3) M. R. Willcott, Ph.D. Dissertation, Yale University, 1962.

(4) A. Tulinsky and R. F. Davis, unpublished work.

(5) K. Alder, R. Muders, W. Krane and P. Wirtz, *Ann.*, **627**, 59 (1959).

(6) J. L. K. Sixma and E. Detilleux, *Rec. trav. chim.*, **72**, 173 (1953).

(7) W. Braren and E. Buchner, *Ber.*, **34**, 982 (1901).

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

(9) A. Harrison, L. Honnen, H. Dauben and F. Lossing, *J. Am. Chem. Soc.*, **82**, 5593 (1960).

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

ments were obtained from the output of a mechanical integrator coupled to the recording potentiometer.

Nitrogen-tropilidene and nitric oxide-tropilidene reactant mixtures were prepared in a storage flask equipped with a magnetically driven glass paddle stirrer. The reaction vessel was packed with 4-mm. dia. soft glass beads which increased the surface to volume ratio by a factor of about 55 relative to the unpacked vessel in a test for surface effects.

Results

After the products were frozen out of the reaction vessel, the products were thawed and the pressure in the manifold was measured in many of the runs before analysis. The ratio of reaction mixture pressure in the manifold to initial reactant pressure in the reaction vessel gives a good indication of any appreciable loss of material through polymerization reactions. No such polymerization was indicated. In one series of eight runs ranging between 20% and 95% conversion this ratio was constant to within the precision of pressure measurement in the 3-mm. region, or 10%. Calculated first-order rate constants were independent of pressure in the maximum pressure range covered, between 0.9 and 19.7 mm. at 369.8°. Most runs were made with reactant pressures between 3 and 5 mm. The calculated first-order rate constants were constant to $\pm 2\%$ between 34% and 84% conversion in the series of four runs at 395.0°, and were constant with maximum deviations of $\pm 10\%$ in another series of nine runs at 383.6° between 20% and 85% conversion. A tenth run at 95% conversion, a degree of reaction for which the exact value of the vessel inlet dead volume correction is most crucial, deviated by 14% from the mean. Thus it is concluded that the reaction is first order.

Three runs were made with a 20:1 ratio of nitrogen to reactant at a reactant pressure of 7 mm. in order to test for any diffusion-controlled wall reactions. The average of the rate constants for these runs was within 1% of the average for the runs without added nitrogen; hence diffusion to and from the walls is not involved in the total reaction. Changing the surface to volume ratio by a factor of 55 by packing the vessel with glass beads also served to decrease the constants by only 3% below the value expected from the Arrhenius plots. Hence it is concluded that surface reactions are unimportant. Addition of nitric oxide in two runs at pressures of 6 and 4 mm. likewise had a negligible effect on the rate constant at 369°.

Rate constants from between four and ten runs at each of five temperatures using the unpacked vessel were averaged to provide values for the Arrhenius plot, Fig. 1. The first-order rate constant is then expressed in the Arrhenius form: $k = 3.5 \times 10^{13} \exp [(-51.1 \pm 0.8) \text{ kcal./RT}] \text{ sec.}^{-1}$. The data are tabulated in the Appendix.

Discussion

A chain process to be considered for this isomerization involving benzyl radicals or isomeric C_7H_7 species as the chain carrier requires a rate of propagation first order in benzyl and first order in tropilidene. The usual steady state approximation for the C_7H_7 concentration is made here. The observed first-order nature of the reaction then requires that benzyl concentration remain constant to better than 10% over at least two half-lives of reactant. If chains are initiated through a homogeneous fragmentation of tropilidene, then the termination reaction must be of the same order in tropilidene as the initiation step to maintain a constant intermediate concentration. Chain initiation through an impurity in the starting material should also fail

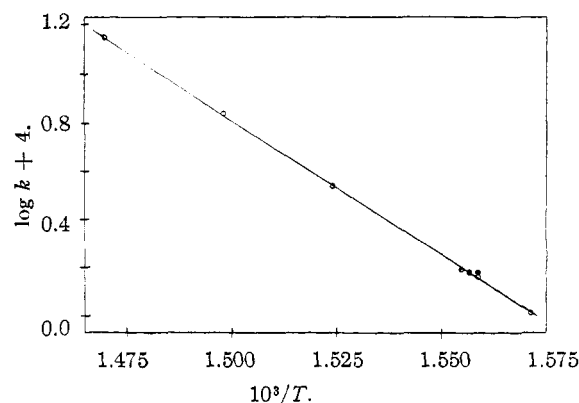


Fig. 1.—Arrhenius plot of averaged rate constants: ○, unpacked vessel, no added gases; ○, packed vessel; ●, NO added.

to give first-order kinetics over wide ranges of conversion as the impurity is consumed unless there is no termination step for the radical intermediates. Different batches of starting material with slightly differing purities gave consistent kinetic data; hence impurities are not considered to be involved in reaction chains.

The absence of surface catalysis, and the lack of effect of nitric oxide coupled with the pressure independence of first-order rate constants for the reaction therefore seem to indicate a non-chain homogeneous process for the tropilidene-toluene reaction. Absence of effect of inert gas addition also indicates the lack of diffusion-controlled wall processes.

It is then fruitful to consider what unimolecular processes are possible with a 51 kcal./mole activation energy. Bent¹¹ lists a figure of 92 kcal. for the strength of an sp^2-sp^3 carbon-carbon bond such as the 1,7-bond in tropilidene. If this figure is reduced by as much as 20 kcal./mole to allow for allylic resonance in the 5,6,7-carbon part of the molecule on rupture of the 1-7 bond, the resulting 70 kcal. bond strength is still well above the observed barrier of 51 kcal. Hence the isomerization cannot involve formation of a diradical species such as



with subsequent hydrogen atom migration and ring closure.

A more complex initial step than a simple carbon-carbon bond rupture must now be considered. Any attempt to picture a concerted process leads one through a state which is formally quite similar to the previously mentioned norcaradiene. It is then worthwhile to estimate the standard free energy difference for the cycloheptatriene-tropilidene reaction. The standard free energy of formation of gaseous norcaradiene at 25° has been determined to be 61.0 kcal./mole.¹² Franklin's method of group equivalents¹³ can be used to compute the free energy of formation of gaseous norcaradiene at 25° using contributions for two *cis*- C_2H_2 groups, two CH groups, one CH_2 group, the cyclopropane correction, and the cyclo- C_6 correction, yielding a value of +73.0 kcal. Therefore $\Delta F^\circ_{25} = +12$ kcal./mole for the reaction; ΔH° is found to be +11 kcal./mole by a similar calculation. Allowing an error of ± 5 kcal. for the norcaradiene computation, cycloheptatriene is seen to be by far the dominant species

(11) H. Bent, *Chem. Revs.*, **61**, 295 (1961).

(12) H. Finke, D. Scott, M. Gross, J. Messerly and G. Waddington, *J. Am. Chem. Soc.*, **78**, 5469 (1956).

(13) J. L. Franklin, *Ind. Eng. Chem.*, **41**, 1070 (1949).

in tropilidene. If the activation energy were even as much as 30 kcal. greater than the endothermicity for the cycloheptatriene-norcaradiene valence tautomerism reaction, a normal pre-exponential factor would result in a rate of attainment of a cycloheptatriene-norcaradiene equilibrium which would be quite rapid compared to the over-all rate of conversion to toluene. The rearrangement of the norcaradiene species to toluene must then take place with an activation energy of $51 - 11 = 40 \pm 5$ kcal./mole, and a pre-exponential factor of about $(3 \pm 2) \times 10^{13}$ sec.⁻¹. Simple cyclopropane isomerizations to propylenes and alkyl substituted propylenes take place with activation energies of around 65 kcal.,^{14,15} and it seems reasonable that benzene ring formation would aid the hydrogen migration and ring opening to the extent of 20-25 kcal./mole. Alternately, the opening of the bicyclic cyclopropane ring yields an allylic radical stabilized by about 20 kcal./mole relative to such an opening in simple cyclopropanes.

In the study of the kinetics of the thermal decomposition of (2,2,1)bicycloheptadiene¹⁰ it was noted that toluene was also produced in yields of 6-7% of the tropilidene. Based on that data it was not feasible to assert whether the toluene was a primary product of the bicycloheptadiene decomposition or a product of the tropilidene reaction because of uncertainty in the tropilidene analyses at low conversions. It is now possible to make a direct comparison of the results of both sets of data. At 370°, tropilidene is 5% converted to toluene in 340 sec. In the experiments with the bicyclo compound at 370°, the toluene/tropilidene ratio was 0.062 ± 0.010 after times between 130 and 200 sec. It then appears likely that some toluene is formed directly from bicycloheptadiene. One reference to the contrary is a footnote referring to unpublished work by an anonymous referee¹⁶ who is quoted as having shown that the toluene comes only from the tropilidene. No details are given, and without quantitative kinetic studies it is difficult to see how this conclusion could be reached.

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(16) S. Myerson, J. McCollum and P. Rylander, *ibid.*, **83**, 1401 (1961), ref. 23.

Appendix

A. Data for runs without added gases; α = fraction reactant left

$T, ^\circ\text{C.}$	Reactant $P, \text{ mm.}$	α	$k \times 10^4,$ sec. ⁻¹
362.8	6.0	0.86	0.84
	4.0	.75	0.96
	2.6	.89	1.08
	2.3	.73	1.23
	1.6	.82	1.32
	2.1	.54	1.06
	11.1	.78	0.99
	0.5	.79	0.85
368.2	4.5	.75	1.39
	3.5	.78	1.42
369.2	4.8	.75	1.56
	2.2	.66	1.51
	3.3	.44	1.52
	2.3	.57	1.52
	19.7	.76	1.54
	7.0	.77	1.50
	0.9	.76	1.47
370.0	3.6	.68	1.54
	7.3	.75	1.54
	6.4	.72	1.56
	4.4	.78	1.63
383.0	2.0	.80	3.27
	3.0	.61	3.42
	1.9	.53	3.54
	2.5	.59	3.46
	3.9	.28	3.54
	2.4	.28	3.57
	3.7	.055	4.04
	3.7	.13	3.80
	3.2	.33	3.52
	3.4	.78	3.26
394.3	3.9	.66	6.88
	3.0	.43	7.05
	2.9	.28	7.13
407.3	4.0	.16	6.78
	3.7	.25	14.8
	3.0	.41	13.8
	2.9	.64	13.8
	2.9	.32	13.8

B. Data for runs with added gases

368.2	6.7 + 5.8 mm. NO	0.77	1.42
	4.5 + 4.0 mm. NO	.79	1.55
383.0	2.2 + 85 mm. N ₂	.81	3.32
	6.9 + 123 mm. N ₂	.29	3.41
	6.0 + 111 mm. N ₂	.50	3.69
	7.0 + 141 mm. N ₂	.66	3.60