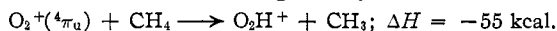
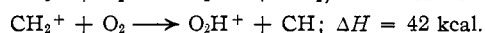
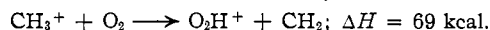
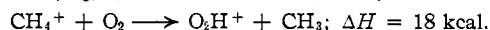
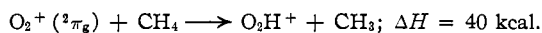


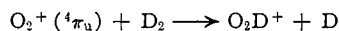
are excited, $P_L\sigma_{L,obsd.}$ will be less than $\sigma_{L,calcd.}$. Earlier work assigns H_2^+ as the reactant ion.^{11,12} Although the appearance potentials of O_2H^+ and H_2^+ coincide, the first excited state of O_2^+ also matches¹³ and is therefore allowed. The formation of O_2H^+ in a mixture of oxygen and methane requires excited O_2^+ for the reaction to be energetically allowed.¹⁴



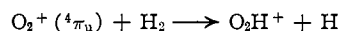
The following reactions are endothermic and are presumed not to occur.



Another fact which strongly supports the choice of O_2^{+*} is that E_t is observed graphically, and is in the measurable range of E_0 , for



but not for



Replacing H_2 by D_2 as the *molecule* will lower the value of E_t by about a factor of two but is expected to have little effect if H_2^+ and D_2^+ are involved. This is evident on inspecting equations 3 and 4.

This feature of being unable to observe graphically a discontinuity associated with E_t also applies to mixtures of light and heavy hydrogen with argon, nitrogen or carbon monoxide. According to equation 3 the combination of large σ_L and small σ_K dictates a large E_t . Values of Q for the $N_2 + H_2$ and $N_2 + D_2$ systems were re-examined at higher E_0 by using additional batteries in the repeller voltage circuit. E_t was then observed for both mixtures. The calculated ratio $E_{t,H_2}/E_{t,D_2}$ from equations 3 and 4 is 1.88; the observed ratio is 2.1.

Another test of our description is to compare σ_K obtained from

(11) D. P. Stevenson and D. O. Schissler, *J. Chem. Phys.*, **29**, 282 (1957).

(12) P. Dong and M. Cottin, *J. chim. phys.*, **57**, 557 (1960).

(13) D. C. Frost and C. A. McDowell, *J. Am. Chem. Soc.*, **80**, 6183 (1958).

(14) Values of ΔH_f are taken from F. H. Field and J. L. Franklin, "Electron Impact Phenomena," Academic Press, Inc., New York, N. Y., 1957.

$$\sigma_K = \sigma_L/E_t^{1/2} \quad (13)$$

with values calculated from van der Waals equation, σ_{vdw} , gas viscosity, σ_{gv} , and molar refraction, σ_{mr} . These comparisons appear in Table III. The values of σ_K are very plausible and in fact appear to reflect the differences between the molecules more faithfully than do the other σ 's.

TABLE III
VALUES OF E_t AND σ_K

Ion	Molecule	$E_t^{1/2}$, ev. ^{1/2}	$\sigma_{K,obsd.}$, Å. ²	σ_{Kgv} , Å. ²	σ_{Kvdw} , Å. ²	σ_{Kmr} , Å. ²
D ₂	D ₂	2.64	8	18.3	24	10.8
H ₂	H ₂	2.60	8.1	18.3	24	10.8
D ₂	H ₂	2.42	10.7	18.3	24	10.8
H ₂ O	D ₂	1.57	22.2	18.8	25	13.3
D ₂ O	H ₂	2.76	17.2	18.8	25	13.3
H ₂ O	n-C ₄ D ₁₀	2.00	27.5	34.8	44	31.6
CD ₄	CD ₄	1.65	23	31.4	33	24.2
CD ₃	CD ₄	1.75	21.2	31.4	33	24.2

Values of P_L obtained from the comparison of $\sigma_{L,calcd.}$ and $P_L\sigma_{L,obsd.}$ are unity for most of the reactions studied. Values of P_K , however, are not reliable due to the cumulative errors in determining E_t , slopes and intercepts. The reproducibility of replicate measurements is indicated in Table IV for the hydrogen self reaction.

TABLE IV

REPRODUCIBILITY OF REPLICATE MEASUREMENTS FOR THE HYDROGEN SELF REACTION

Slope of Q vs. E_0^{-1} , Å. ² ev.	Intercept of Q vs. E_0^{-1} , Å. ²
65.5	5
64.1	5
65.6	10
60.5	11

Unpublished work of Dr. T. F. Moran¹⁵ in this laboratory with molecules possessing permanent dipole moments have indicated a "locking-in" effect which greatly enhances the observed cross section. The present results do not indicate analogous "locking-in" of the ion on a particular orientation of the induced dipole of the molecule.

(15) T. F. Moran, Ph.D. Thesis, University of Notre Dame, 1962.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, LOS ANGELES STATE COLLEGE, LOS ANGELES, CALIF.]

The Effect of Certain Variables on the Ultrasonic Cleavage of Phenol and of Pyridine¹

BY DOUGLAS L. CURRELL, GEORGE WILHEIM AND SZABOLCS NAGY

RECEIVED JULY 23, 1962

The effect of pH and dissolved gases on the ultrasonic reaction of aqueous solutions of phenol and of pyridine to produce acetylene has been investigated. Phenol in alkaline solution and pyridine in acid solution are essentially unaffected by ultrasonic waves. The rate of production of acetylene is dependent upon the ratio of specific heats of the dissolved gases. The rate of the ultrasonic cleavage of the pyridine ring was shown to be independent of the surface tension of the reaction solution. The significance of these results is discussed in terms of possible mechanisms for the chemical effect of ultrasonic waves.

Introduction

Current theories as to the mechanism by which ultrasonic waves bring about chemical change² involve the phenomenon of cavitation, *i.e.*, the formation of bubbles in a liquid system subjected to an intense

ultrasonic beam. When the applied ultrasonic beam is of an intensity insufficient to produce cavitation, no chemical change is observed. Further, it appears the presence of a dissolved gas whose function is to furnish nuclei is necessary for the occurrence of cavitation.

From experiments on the effect of dissolved gases on the ultrasonic reaction, Griffing³ has proposed that

(1) Presented at the Pacific Southwest Regional Meeting of the American Chemical Society, Los Angeles, Calif., December, 1960. This research was supported by the Directorate of Chemical Sciences, Air Force Office of Scientific Research.

(2) For leading references *cf.* A. Weissler, *J. Am. Chem. Soc.*, **81**, 1077 (1959).

(3) V. Griffing, *J. Chem. Phys.*, **20**, 939 (1952); M. E. Fitzgerald, V. Griffing and J. Sullivan, *ibid.*, **25**, 926 (1956).

the chemical reactions take place inside the gas bubbles formed in the ultrasonic field. A corollary of this theory is that in order to be affected by ultrasonic waves, a substance must have sufficient vapor pressure to occur in significant concentration in the bubble. It follows that the ultrasonic reactions of solutions of organic acids and bases should be sensitive to changes in pH since the formation of a salt of either would preclude entrance into the bubble.

Based on a study of the effect of surface tension of a liquid on the cavitation pitting action at an aluminum surface, Hueter and Bolt⁴ have suggested that the higher the surface tension of the reaction solution, the greater the amount of energy released upon collapse of the cavitation bubble since the energy so released should depend on the work required to form a new surface in the expansion of the bubble. Thus, the greater the surface tension of the reaction solution, the faster should be the rate of the ultrasonic reaction.

To test these hypotheses, the effect of pH and surface tension on the rate of production of acetylene in the ultrasonic reactions of aqueous solutions of phenol and of pyridine has been examined. These reactions were first reported by Zechmeister and his collaborators.^{5,6} It was reported earlier⁶ that the rate of production of acetylene in the ultrasonic cleavage of pyridine was accelerated in the presence of argon. These experiments have now been extended to include phenol and pyridine in other gaseous atmospheres.

Experimental

Materials and Methods.—Analytical reagent phenol and pyridine were obtained from the Mallinckrodt Chemical Works and used without further purification. The following gases were obtained from the Matheson Co.: argon (99.998%), helium (99.99%), oxygen (99.6%), sulfur hexafluoride (98.0%). The following surface active substances were used: GE Antifoam 60 from the General Electric Co.,⁷ Igepon AC-78 (sodium β -laurylethanesulfonate, 83% minimum) from Antara Chemicals, Fluorochemical FC-126 (ammonium perfluoro-caprylate) from the Minnesota Mining and Manufacturing Co.

Two ultrasonic generators were used: a Brush Electronics Co. (Cleveland, O.) hypersonic generator model BU-204 (250 watts, 1000 kilocycles per sec.) for experiments involving pyridine and a McKenna Laboratories (Santa Monica, Calif.) model EB240 ultrasonic generator (240 watts, 1000 kilocycles per sec.) for phenol. The transducer elements were cup-shaped, 9 cm. in diameter and were of barium titanate with a ceramic glaze.

The reactions were carried out in 100-ml. round-bottom Pyrex flasks with necks 22 cm. long and fitted with a gas inlet tube (diam., 6 mm.) whose tip was 2 cm. above the surface of the liquid.⁸ The same individual flask was used in parallel runs. The reaction flask was immersed in water covering the transducer element and was surrounded by cooling coils through which water was passed at a rate which maintained a temperature of approximately 40° inside the reaction flask. The transducer was supported by a Labjack which permitted adjustment of its position relative to the flask until maximum fountain height was observed.

The reaction vessel containing 50 ml. of the aqueous solution was swept continuously (as well as 5 min. before and after) during the ultrasonic treatment at a rate of approximately 24 cc./min. In order to analyze for acetylene, the gaseous products were swept into three tubes containing ammoniacal cuprous solution prepared according to Ilosvay.⁹ The sweep gas was argon in all cases except those in which the effect of dissolved gases was being studied. The cuprous acetylide formed was analyzed as described by Willstätter and Maschmann.¹⁰

Each determination was made a minimum of three times; the average error was approximately 10%.

(4) T. F. Hueter and R. H. Bolt, "Sonics," John Wiley and Sons, Inc., New York, N. Y., 1955, p. 238.

(5) L. Zechmeister and E. F. Magoon, *J. Am. Chem. Soc.*, **78**, 2149 (1956).

(6) D. L. Currell and L. Zechmeister, *ibid.*, **80**, 205 (1958).

(7) Containing 20–40% of a methylpolysiloxane, 0.5% silica, 40–65% water, 4–8% of the monostearic acid ester of polyethyleneglycol and 6–10% of the monostearic acid ester of sorbitol.

(8) For a sketch of the apparatus cf. L. Zechmeister and E. F. Magoon, "Festschrift Arthur Stoll," Birkhäuser, Basel, 1957, p. 59.

(9) L. von Ilosvay, *Ber.*, **32**, 2697 (1899).

(10) R. Willstätter and E. Maschmann, *ibid.*, **53**, 939 (1920).

In some experiments involving phenol, 0.85 g. (5.0 mmoles) of silver nitrate was dissolved in the reaction solution since, as reported earlier,⁹ the yield of acetylene from phenol is much higher in the presence of silver nitrate. The silver acetylide thus obtained was converted into cuprous acetylide and analyzed as described by Zechmeister and Wallcave.¹¹ A similar procedure was followed in the ultrasonic treatment of pyridine in an oxygen atmosphere.

To determine whether silver acetylide was reacting with oxygen to produce carbon dioxide in the presence of oxygen, an aqueous solution of pyridine and silver nitrate was treated for 9 hours in the presence of argon. The silver acetylide suspension thus produced was swept with oxygen for 12 hours. That no carbon dioxide had been formed was shown by the absence of a precipitate in a solution of barium hydroxide through which the oxygen was passed.

The determination of phenol was carried out by titration with standard bromine.¹²

Pyridine was analyzed through precipitation as pyridinium tetraphenylborate according to a modification of Crane's procedure.¹³ To a solution containing 50 ml. of water, 0.20 ml. of concd. sulfuric acid and 0.20 ml. of pyridine was added 10 ml. of a solution containing 10 g. of sodium tetraphenylborate per 100 ml. of solution. After standing for 3 hr., the pyridinium tetraphenylborate was removed by filtration through a tared crucible, washed with water, and dried to constant weight *in vacuo* at room temperature. The average of several results indicated that under these conditions precipitation was 89% complete. Before the procedure was applied to the reaction solutions, it was necessary to filter off the dark-brown precipitate described earlier.⁶ It should be emphasized that this method allows only a crude approximation to the amount of pyridine remaining in the reaction solution since it suffers from possible interference by the reaction products present.

In order to analyze for carbon dioxide as barium carbonate, the gaseous products were swept from the reaction flask continuously during the ultrasonic reaction into barium hydroxide solution.

Effect of pH .—To determine the effect of acid on the ultrasonic reaction of pyridine, 0.20 ml. (0.37 g., 3.8 mmoles) of sulfuric or phosphoric acid was added to 50 ml. of an aqueous solution containing 0.20 ml. (2.5 mmoles) of pyridine. After ultrasonic treatment for 10 hr., the solution was made alkaline to litmus by the addition of sodium hydroxide pellets before continuing the ultrasonic treatment.

In experiments involving the effect of base on the ultrasonic reaction of phenol, sodium hydroxide (1.0 g., 2.5 mmole) was added to 50 ml. of an aqueous solution containing 0.20 g. (2.1 mmoles) of phenol. After a 9-hr. treatment, the reaction solution was made acid to litmus by the addition of sulfuric acid (1 ml. in excess) before continuing the treatment.

Effect of Surface Tension.—The surface active substances used met two requirements: (1) they were solid in order to minimize entrance into the bubble and resultant interference with the ultrasonic reaction; (2) they produced reaction solutions with pH of 7.0 ± 0.2 in order to minimize the formation of pyridinium salts. The surface tension measurements were made at 32° with a Du Nuoy surface tension apparatus.

Discussion and Results

Effect of pH .—The results in Table I show that when pyridine is converted into the pyridinium salt in acid solution, and when phenol is converted into sodium

TABLE I
EFFECT OF pH ON THE ULTRASONIC REACTION OF AQUEOUS SOLUTIONS OF PHENOL (2.1 MMOLES) AND PYRIDINE (2.5 MMOLES) IN AN ARGON ATMOSPHERE

Acid or base present in excess	C ₂ H ₂ formed during first 10 hr., ^a mg.	C ₂ H ₂ formed during second 10 hr., ^a mg.	% C-atoms recovd. as C ₂ H ₂ at end of 30 hr. treatment
Pyridine			
H ₂ SO ₄	Trace	11.5	10.6
H ₃ PO ₄	Trace	14.8	13.2
None	16.8	..	14.5
Phenol			
NaOH	Trace ^b	8.3 ^b	
None		6.2 ^b	

^a After making the solution alkaline (for pyridine) or acidic (for phenol). ^b 9-hr. periods of treatment.

(11) L. Zechmeister and L. Wallcave, *J. Am. Chem. Soc.*, **77**, 2853 (1955).

(12) W. W. Scott, "Standard Methods of Chemical Analysis," Vol. II, 5th Ed., D. Van Nostrand Co., Inc., Princeton, N. J., 1939.

(13) F. E. Crane, *Anal. Chem.*, **28**, 1794 (1956).

phenoxide in basic solution, the ultrasonic cleavage of the ring to produce acetylene is only barely detectable.

The best explanation for these results appears to be that formation of the pyridinium and phenoxide salts has reduced the vapor pressure of the reactants to such an extent that they are unable to enter the bubbles present and are, hence, unaffected by the ultrasonic waves. These results provide an explanation for the previously reported⁶ retardation of the ultrasonic cleavage of pyridine by silver nitrate, since the latter provides an acidic reaction medium.

To rule out the possibility of a reaction other than acetylene formation, it seemed important to demonstrate that the pyridine and phenol remained unchanged during the ultrasonic treatment. The pyridine and phenol remaining unchanged after 10- and 9-hour treatments proved to be 99% and 91%, respectively. By contrast, only 63% of free phenol remained unchanged after a 9-hour treatment. Further, when the pyridine or phenol were freed from their salts following the initial ultrasonic treatment and the solution was treated further with ultrasonic waves, the expected reaction to produce acetylene took place (Table I).

The pyridine reaction was unaffected by the presence of base and the phenol reaction was unaffected by the presence of acid, thus ruling out the possibility that the results were due to reaction of the acid or base with intermediates or products of the reaction.

Effect of Surface Tension.—The results in Table II show that the surface tension of the reaction solution had no appreciable effect on the rate at which acetylene is produced in the ultrasonic reaction of pyridine. It was expected that lowering the surface tension of the reaction solution would result in a decrease in the rate of production of acetylene. A possible explanation for these results is that in the solutions of lower surface tension more bubbles form under the influence of the ultrasonic beam. A greater number of bubbles leading to a greater production of acetylene per unit time would, perhaps, compensate for the lower yield of acetylene per bubble.

TABLE II

EFFECT OF SURFACE TENSION ON THE 20 HR. ULTRASONIC TREATMENT OF AQUEOUS SOLUTIONS OF PYRIDINE (2.5 MMOL) IN AN ARGON ATMOSPHERE

Concn. of surface active substance	Surface tension of react. soln., dynes/cm.		Mg	C ₂ H ₂ formed during			% C-atoms recovd. as C ₂ H ₂ at end of 20-hr. treatment
	Before react.	After react.		5 hr.	10 hr.	20 hr.	
None	60.9	49.0	11.1	16.8	23.4	14.5	
0.2% Igepon	35.8	35.4	11.0	16.9	24.9	15.5	
.005% Igepon	48.1	53.8	10.2	15.4	22.5	13.8	
.2% fluorochemical	35.4	57.9	11.3	15.3	18.0	11.1	
.2% silicone	37.7	50.1	10.6	14.5	19.1	11.5	
.005% silicone	56.1	56.5	11.2	16.9	20.2	12.6	

^a The surface tension of all solutions had achieved the terminal value after 10-hr. treatment except for the Fluorochemical whose solution had a surface tension of 25.5 dynes/cm.

Virtanen and Ellfolk report an inhibitory effect of volatile fatty acids on the fixation of nitrogen through the action of ultrasonic waves on water in which air is dissolved.¹⁴ They explain their results as due to the lowering of the surface tension of the water by the fatty acids. In view of our results, a better explanation would seem to be the entrance of the volatile acids into the cavity or bubble and a resulting interference with the reaction. This idea is supported by

(14) A. I. Virtanen and N. Ellfolk, *Acta Chem. Scand.*, **6**, 660 (1952).

the report of these authors that when the fatty acid solution is made alkaline, the inhibition of the reaction becomes slight.

Effect of Dissolved Gases.—Table III shows that the rate of acetylene production from phenol or pyridine is markedly increased in an atmosphere of argon. Grifing, *et al.*, have reported³ a very similar effect of dissolved gases on the rate of liberation of chlorine in the ultrasonic treatment of an aqueous suspension of carbon tetrachloride. These authors have proposed that the ultrasonic reaction occurs within the bubbles formed in the ultrasonic field and is due to high temperatures developed locally during adiabatic compression of the bubble. They point out that a consequence

TABLE III

EFFECT OF SOME DISSOLVED GASES ON THE ULTRASONIC REACTION OF AQUEOUS SOLUTIONS OF PYRIDINE (2.5 MMOL) AND OF PHENOL (2.1 MMOL)

Dissolved gas	C ₂ H ₂ formed during first 10 hr., mg.	% C-atoms		Duration of treatment, hr.	% C-atoms recovd. as CO ₂ at end of treatment
		recovd. as C ₂ H ₂ at end of treatment	recovd. as CO ₂ at end of treatment		
Pyridine					
Argon	16.8	14.5		20	0.3
Helium	6.2	11.2		37	
Nitrogen	6.9	8.0		37	
Sulfur hexafluoride	Trace			10	
Oxygen ^a	Trace			20	15.7
Phenol					
Argon ^a	14.2	16.2		50	1.9 ^c
Helium ^a	6.2			9 ^b	
Nitrogen ^a	2.4			9 ^b	
Sulfur hexafluoride	Trace			9 ^b	
Oxygen ^a	Trace			9 ^b	14.8 ^c

^a In the presence of silver nitrate. ^b Reactions were not run to completion. ^c Based on the amount of phenol reacted.

of this hypothesis is the dependence of the rate of ultrasonic reactions on the ratio of the specific heats of the gases present in the bubbles since this ratio will affect the temperature attained upon compression of the bubbles. The observed difference in the case of the two gases having the same ratio of specific heats, argon and helium, they explain as being due to the greater (tenfold) thermal conductivity of helium.

As shown in Table III, only a trace of acetylene appeared when phenol or pyridine was treated with ultrasonic waves in an atmosphere of sulfur hexafluoride. That the starting materials remained essentially unchanged was shown by continuing the ultrasonic treatment in an argon atmosphere whereby the normal amount of acetylene was liberated. Further, the amount of unchanged pyridine and phenol was determined to be 85% and 99%, respectively. That this behavior, in the case of pyridine, was not due to developing acidity through reaction of the sulfur hexafluoride was shown when the same results were obtained in an alkaline solution. In a similar fashion, it was shown that the relatively low yield of acetylene in a nitrogen atmosphere was not due to developing acidity although nitrogen as a reactant in this case cannot be excluded.¹⁵

The results in an atmosphere of oxygen (Table III) cannot be explained upon the basis of ratio of specific heats since oxygen has a ratio close to that of nitrogen. Neither phenol nor pyridine remained unchanged in the ultrasonic treatment in the presence of oxygen since further treatment in an argon atmosphere produced no

(15) For a case in which nitrogen does participate as a reactant *cf.* ref. 14.

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.

[CONTRIBUTION NO. 1705 FROM THE STERLING CHEMISTRY LABORATORY, YALE UNIVERSITY, NEW HAVEN, CONN.]

The Thermal Isomerization of Tropilidene

BY KIRBY N. KLUMP AND JOHN P. CHESICK¹

RECEIVED JULY 31, 1962

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-tropilidene-carboxylic 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-cyclopropane-dicarboxylic 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-C1 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. Detilleaux, *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).