

in the alkyl chain were unchanged. These spectral features indicated that deuteration had occurred at both the α - and γ -carbons as well as in the methylsulfinyl group. A control reaction was run under identical conditions using *t*-butyl alcohol as solvent. The sulfoxide recovered from this reaction was essentially identical with starting material (n.m.r. and infrared spectra).

Analysis of Equilibrium Mixtures of the Unsaturated Sulfides and Sulfoxides by Oxidative Cleavage.—The procedure of Kuemmel¹⁶ was employed using 2–3 times the prescribed amount of

potassium permanganate. The accuracy of the method was verified with samples of pure α,β -unsaturated sulfides and sulfoxides.

Acknowledgment.—We are indebted to Professor W. von E. Doering for helpful suggestions and discussions during the course of this work, to Dr. T. J. Flautt for help with the n.m.r. spectra, and to Mr. A. L. Voegelé for excellent technical assistance in the laboratory.

[CONTRIBUTION FROM THE NORTH AMERICAN AVIATION SCIENCE CENTER, CANOGA PARK, CALIF.]

The Hydrogen Carrier Technique for the Pyrolysis of Toluene

BY J. G. BURR, R. A. MEYER, AND J. D. STRONG

RECEIVED MARCH 13, 1964

The only products formed from the pyrolysis of toluene at 750° with a hydrogen or deuterium carrier gas are methane and benzene. The apparent activation energy for toluene consumption is 46.1 kcal./mole (log $A = 7.87$). It is concluded that the effect of the carrier gas is to replace the ordinary nonchain toluene pyrolysis mechanism by a chain reaction with hydrogen atoms as the chain carrier. The isotopic compositions of the products formed when toluene- d_8 , ring-deuterated toluene, and methyl-deuterated toluene are pyrolyzed with deuterium or hydrogen as the carrier gas suggest that the difference between C–H and C–D bonds is as important as the difference between ring and side-chain C–H bonds in determining the site of methyl and phenyl radical reactions. Both methyl and phenyl radicals abstract hydrogen preferentially from the toluene ring rather than from the side chain.

Introduction

It was reported earlier¹ that the pyrolysis products of toluene at 750° are reduced to simply methane and benzene if a hydrogen carrier gas is used. It was proposed that at these temperatures, hydrogen could function as a scavenger for benzyl, methyl, and phenyl radicals. Studies were carried out with deuterated toluenes and deuterium as well as hydrogen carrier. These studies have now been extended to the use of ring-deuterated toluene, with both hydrogen and deuterium carriers. The studies reported earlier have been repeated at a higher degree of toluene conversion in order to measure the effect of this variable on the distribution of deuterium in the pyrolysis products.

In agreement with other literature on this hydrogenolysis,² we now believe that the hydrogenolysis proceeds *via* a chain mechanism,^{2a} with hydrogen atoms as chain carriers. Our measurement of the over-all apparent activation energy, 46.1 kcal./mole, is in agreement with such a mechanism and with previous measurements of this quantity, 45^{2b} and 43^{2a} kcal./mole. The isotope data reported in this paper will therefore be discussed in terms of such a mechanism.

Experimental

Apparatus.—The equipment train used is similar to that described earlier¹ but more elaborate. It is shown diagrammatically in Fig. 1.

Temperatures were measured with a thermocouple in a well inserted down the middle of the quartz reactor and read with a potentiometer; the temperature of the furnace was controlled by another thermocouple placed between the quartz reactor and the inner wall of the tube furnace and connected to a temperature controller. This is a more precise way of measuring

and controlling temperature than that used earlier¹ where the thermocouple in the reactor well was attached to the controller, and the temperature was read off of the controller. Inasmuch as the results obtained at an indicated temperature of 750° in the earlier set-up look like the results obtained at about 700° with the present set-up (runs 9 and 19, Table II), we conclude that the indicated temperature in our earlier report¹ was about 50° too high.

Materials.—Toluene- d_8 and toluene- d_4 were from Merck and Co., Canada; the toluene- d_3 contained 7.4% toluene- d_2 and the toluene- d_4 contained 6.1% toluene- d_7 . The toluene- d_8 was prepared in this laboratory from benzene- d_6 . The product was purified gas chromatographically and contained 5.7% toluene- d_4 by low voltage mass spectrometry. The mass pattern of the toluene- d_8 has points of interest and has been discussed recently.³

Procedures and Analyses.—The conditions of operation were kept closely similar for all of the runs described here. Weights of toluene (or deuterated toluenes) were very close to 250 mg. (2.6 minoles). The flow rates of carrier gas ranged from 70–110 ml./min. (except runs 17 and 18 where they were about 150 ml./min.). The gas mixture was introduced at atmospheric pressure into the flow system. The differences in flow rate affected only the contact times and percentage conversions, but did not affect the rates. The total volumes of gas passed were in the range of 2900–3300 ml. It was found that gas flow was considerably slower while the frit was wet with toluene than after the toluene had been evaporated. Duration of a run was measured from the appearance of methane to the disappearance of methane in the effluent gas (15–25 min.). Toluene concentrations in the reaction zone were calculated from the total volume of toluene vapor and the total volume of gas passed, and averaged 6–8% for most runs. Total conversions of toluene were 5–8% for runs at 750°, 2% for the low temperature run (20), and 15% for the high temperature run (21). The recovery of toluene was usually in excess of 90% of the amount charged.

Methane yield was measured by sampling the effluent gas stream approximately every minute with the gas chromatograph. The methane content of the stream thus measured was expressed as μ l. of methane per 5-cc. sample, and these numbers were plotted as a function of time (with the injection of toluene into the frit as the zero time). The area under the curve was integrated gravimetrically to calculate the total yield of methane. The chromatograph was calibrated with a 1% blend of methane in hydrogen.

Isotopic composition of the methane was measured by recovering the methane collected in the charcoal trap and analyzing it in a CEC 103 mass spectrometer. The methane was recovered

¹ R. A. Meyer and J. G. Burr, *J. Am. Chem. Soc.*, **85**, 478 (1963).

² (a) H. Matsui, A. Amano, and H. Tokuhisa, *Bull. Japan. Petrol. Inst.*, **1**, 67 (1959); (b) R. I. Silsby and E. W. Sawyer, *J. Appl. Chem.*, **6**, 347 (1956); (c) H. Morii, A. Hashimoto, and H. Tominga, *Proc. World Petrol. Congress*, 6th Congress, Section IV, paper 24, June, 1963; British Patent 7,121,440. We regret the neglect of these papers in our earlier communication.¹ (d) Abstracts, 1963 American Chemical Society Summer Symposium on Unimolecular Reactions in the Mass Spectrometer, J. G. Burr and R. A. Meyer, *J. Chem. Phys.*, **40**, 2046 (1964).

TABLE I
 RATES OF PRODUCT FORMATION IN THE PYROLYSIS OF TOLUENES

Run	Sample	Carrier gas	T, °C	Residence time, sec.	% conversion/sec. to		Toluene, moles/l. × 10 ³	R(toluene) moles/l.-sec. × 10 ⁴
					Methane	Benzene		
20	C ₆ H ₅ CH ₃	H ₂	707	2.43	0.683	0.412	0.754	4.132
15	C ₆ H ₅ CH ₃	H ₂	751	4.38	1.130	1.374	.930	11.6
16	C ₆ H ₅ CH ₃	H ₂	751	3.03	1.482	1.017	.901	11.3
21	C ₆ H ₅ CH ₃	H ₂	804	3.4	4.51	3.609	.852	34.6
9	C ₆ H ₅ CH ₃	D ₂	757	4.95	1.353	0.703	.795	8.17
12	C ₆ H ₅ CD ₃	H ₂	751	6.56	1.328772	10.3
10	C ₆ H ₅ CD ₃	D ₂	756	5.18	1.110	0.630	.857	7.47
11	C ₆ H ₅ CD ₃	D ₂	752	5.02	1.050844	8.86
13	C ₆ H ₅ CH ₃	H ₂	750	5.84	1.281	0.800	.782	8.14
14	C ₆ H ₅ CH ₃	H ₂	751	6.25	1.269	.853	.882	9.36
17	C ₆ D ₅ CH ₃	D ₂	751	4.0	0.67	(.135) ^a	.965	6.47
18	C ₆ H ₅ CH ₃	D ₂	755	3.2	0.73	.475	.905	5.48
36	C ₆ D ₅ CD ₃ ^a	H ₂	707	3.56	1.26	1.04	1.077	12.4
37	C ₆ D ₅ CD ₃ ^a	H ₂	754	3.56	3.59	2.66	1.093	34.1

^a This toluene contained 2.2% benzene and four other impurities totaling 1%. The numbers in column 7 are corrected for this amount of benzene. Following runs 36 and 37, the concentration of impurities other than benzene had decreased to 0.43%. We think that the high rate of toluene conversion (column 9) is a reflection of these impurities.

from the trap by attaching the trap to a vacuum line, pumping on the trap first at -196° , then at -30° (to remove most of the hydrogen), and finally heating the trap to about 300° and removing the methane with a Toepler pump into a gas sample holder.

Benzene yield was determined by gas chromatographing the condensate from the annular trap (TR₁ of the equipment train, Fig. 1) using a 2.5-m. Ucon 50-HB-2000 column. The efficiency of benzene collection from a standard sample put through the train was found to be over 98%. A sample of the benzene in the condensate was isolated with an Autoprep gas chromatograph, and a Hamilton fraction collector, and analyzed mass spectrometrically for deuterated species. The isotopic compositions of the toluenes were determined in the same way.

Results

Product Yields.—Gas chromatograms (Loenco-15) of the liquid pyrolysis products and mass spectrograms of the gaseous products showed that methane and benzene were the only detectable pyrolysis products. Ethane, ethylene, acetylene, the xylenes, ethylbenzene, bibenzyl, and biphenyl were specifically absent. Under such conditions the yield of methane should equal the yield of benzene, and the yield of each should equal the consumption of toluene. The yields of methane and benzene and the consumption of toluene (taken as the average of the methane and benzene yields) are shown in Table I, along with the pertinent reaction conditions. The yields of benzene are consistently less than the yields of methane.

The Isotopic Composition of the Products.—These are shown in Table II. The distribution of isotopic species for toluene and toluene-*d*₃ is very similar to that reported earlier,¹ except that the greater fraction of toluene conversion has obviously been reflected in a greater amount of deuterium-hydrogen exchange in the recovered toluene and in the methane-benzene products. Data from runs where hydrogen was the carrier gas are reasonably similar to the earlier data,¹ so it can be judged that the principal effect of the increased conversion reported here is simply the side effect of deuterium-hydrogen exchange. Data for toluene-*d*₃ plus H₂ or D₂ are reported here for the first time.

Apparent Activation Energy.—The entries in columns 6 and 7 of Table I represents the rate constants for product formation, since the reaction is first order in toluene^{2a}; the average of the two entries for each run

is taken as the first-order rate constant for toluene consumption. The semilog plot of these constants (runs 15, 16, 20, 21) vs. $1/T, ^{\circ}\text{K}$. gives a line whose

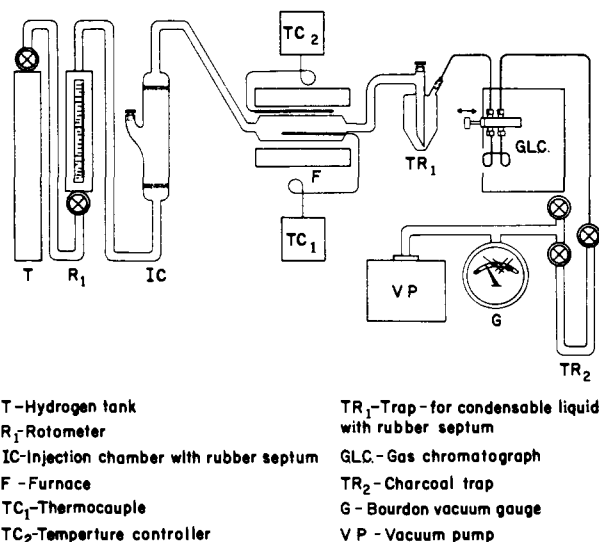


Figure 1.

slope indicates an apparent activation energy of 46 kcal./mole. The rate of toluene consumption at 751° (Table I, column 9) gives a value for A of 6×10^7 sec.⁻¹. The value of E_A is in excellent agreement with literature values.^{2a,b} The value of A compares with the reported values of 10^9 by Matsui, *et al.*,^{2a} and 10^8 by Silsby and Sawyer.^{2b}

Discussion

The pyrolysis of toluene vapor with a hydrogen carrier gives different results from pyrolysis of pure toluene vapor or toluene vapor with an inert gas carrier. The only products from pyrolysis of toluene vapor with a hydrogen carrier are methane and benzene (and probably hydrogen, which is not measurable in this system), whereas in the pyrolysis of pure toluene, hydrogen,³ methane,³ benzene,³ bibenzyl,³ dimethylbiphenyl,³ ethane, and ethylene^{4,5} have been

(3) (a) H. Blades, A. T. Blades, and E. W. R. Steacie, *Can. J. Chem.*, **32**, 298 (1953); (b) M. Szwarc, *J. Chem. Phys.*, **16**, 128 (1948).

(4) M. Takahashi, *Bull. Chem. Soc. Japan*, **33**, 801 (1960).

(5) S. J. Price, *Can. J. Chem.*, **40**, 1310 (1962).

TABLE II
 ISOTOPIC COMPOSITION OF PRODUCTS FROM PYROLYSIS OF TOLUENES AT 750°

Run	Sample	Carrier gas	Subst.	Substance, %							
				d_0	d_1	d_2	d_3	d_4	d_5	d_7	
9 (750°)	$C_6H_5CH_3$	D_2	Methane ^a	8.0	86.4	5.3	0.2				
			Benzene	16.6	59.3	20.3	2.1				
			Toluene	64.9	27.9	6.3					
19 (700°)	$C_6H_5CH_3$	D_2	Methane	5.2	89.5	2.8	1.2	1.3			
			Benzene	25.8	68.7	5.1	0.4				
			Toluene	93.0	6.5	0.6					
12	$C_6H_5CD_3$	H_2	Methane	0	3.9	9.8	86.3				
			Benzene	100							
			Toluene				98				
10, 11	$C_6H_5CD_3$	D_2	Methane	0	1.5	0.7	7.7	90.1			
				0.1	1.7	0.3	8.6	89.3			
			Benzene	16.8	57.8	19.6	4.2				
				17.9	60.2	17.9	3.5				
			Toluene			4.8	68.7	21.3	3.7		
13, 14	$C_6D_5CH_3$	H_2	Methane	100							
			Benzene					3.3	23.0	68.7	5.0
							3.9	24.7	66.4	5.0	
			Toluene				4.1	23.2	72.5		
							4.3	25.5	69.8		
17, 18	$C_6D_5CH_3$	D_2	Methane	5.2	90.9	3.2					
			Benzene						5.6	94.4	
			Toluene					2.5	92.5	4.2	
36 (701°)	$C_6D_5CD_3$	H_2	Methane	1.9	1.0	1.7	93.4	2.1			
37 (754°)	$C_6D_5CD_3$	H_2	Methane	3.1	1.9	5.0	86.8	3.2			
38 (754°)	$C_6D_5CD_3$	H_2	Benzene			0.7	5.2	24.0	50.0	14.7	
			Toluene						1.7	9.4	32.3

(d₈ = 51.0)

^a The isotopic composition of the methane in runs 9 and 19 is different from that reported earlier¹; after several repeat runs, we have concluded that the earlier data are in error.

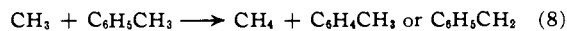
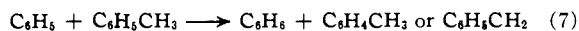
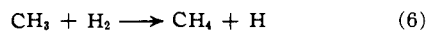
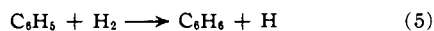
reported. The activation energy for pyrolysis of pure toluene, although in dispute, is about 80–90 kcal./mole, whereas the activation energy for pyrolysis of toluene with a hydrogen carrier is about 43–46 kcal./mole. The pre-exponential factor for pyrolysis of pure toluene is $\log A = 14.8$,³ whereas for the hydrogenolysis process, $\log A = 8$ –9.

These differences are to be expected if the nonchain process for pyrolysis of pure toluene^{3–5} is replaced by a chain process in the presence of excess hydrogen in which hydrogen atoms are the likely chain carriers eq. 1–10.

Initiation:



Propagation:



Termination:



This is essentially the mechanism proposed by Matsui, Amano, and Tokuhisa.^{2a} The result of the isotopic studies reported here have enabled us to add several

steps to the mechanism⁶ and to evaluate the results of competition in several pairs of competitive reactions; e.g., 3 vs. 4, 5 vs. 7, and 6 vs. 8.

This information can be obtained from the data in Table II. This table, however, contains a great deal more information than is needed. We have therefore extracted the significant data from Table II and summarized these in Table III. In each run listed in

TABLE III

SUMMARY OF ISOTOPIC COMPOSITION OF PYROLYSIS PRODUCTS

Sys-tem	Toluene	Carrier gas	Product	Important isotopic species and amount, %	Important reaction
1	$C_6H_5CH_3$	D_2	Methane	CH_4 , 5–8	8
			Benzene	C_6H_6 , 16.6–25.8	7
2	$C_6H_5CD_3$	H_2	Methane	CD_4 , 0	8s
			Benzene	C_6H_5D , 0	7s
3	$C_6H_5CD_3$	D_2	Methane	CD_3H , 8.0	8r
			Benzene	C_6H_6 , 17.3	7r
4	$C_6D_5CH_3$	H_2	Methane	CH_2D , 0	8r
			Benzene	C_6D_6 , 5	7r
5	$C_6D_5CH_3$	D_2	Methane	CH_4 , 5.2	8s
			Benzene	C_6D_5H , 5.6	7s
6	$C_6D_5CD_3$	H_2	Methane	CD_4 , 3	8
			Benzene	C_6D_6 , 15	7

Table II there is only one isotopic species of methane or benzene which is uniquely related to a process shown in eq. 1–10. For example, in run 10, Table II, CD_3H can result only from the reaction of methyl radicals with the toluene ring, reaction 8r (where r

(6) We have adopted this mechanism rather than the one proposed earlier¹ because the observed activation energy of 43–46 kcal./mole is not consistent with a primary split of toluene into phenyl and methyl radicals, but is consistent with a chain mechanism.

or s refer to reaction with ring or methyl group). CD₄, on the other hand, could be the result of either 3 or 8s. CD₄ in run 12 has a unique origin in reaction 8s. The measurement of these two products in the appropriate systems thus provides a measure of methyl radical reactions with the toluene ring and with the toluene methyl group. Other entries in Table III were selected similarly.

Conclusions

A number of conclusions about the importance of various steps in the chain mechanism may be deduced from the entries in Table III: 1. The formation of 16–26% C₆H₆ from pyrolysis of toluene with D₂ (system 1, Table III) and of 15% C₆D₆ from pyrolysis of toluene-d₈ with H₂ (system 6) means that reaction 4 cannot be the only source of benzene, since otherwise only C₆H₅D or C₆D₅H, respectively, would be observed. Reaction 3 must be included, even though Blades and Steacie⁷ did not consider it important in the pyrolysis of pure toluene. Reactions 3 and 4 are thus the sources of phenyl and methyl radicals which disappear by reaction with either the carrier hydrogen or by reaction with either the ring or the methyl group of the toluene. Unfortunately, in the work reported here, there are no products produced which would allow a quantitative comparison of reactions 3 and 4 and so we cannot determine the relative probabilities of 3 vs. 4 from this sort of isotope work. This also means that we cannot estimate the total amount of phenyl or methyl radicals produced under the conditions used here.

2. The products of phenyl reaction with toluene are always more abundant than the products of methyl reaction with toluene. Thus, in system 1, Table III, CH₄ is 8% of the total methane and C₆H₆ is about 20% of the total benzene. If we assume that amounts of phenyl and methyl radicals formed by 3 and 4 are roughly equal, then the numbers in Table III mean that phenyl radicals are more selective than methyl radicals.

3. The site of methyl or phenyl reactions with toluene—namely, ring or methyl group—appears to be governed largely by whether the site is deuterated or not. For example, the reaction of methyl or phenyl radicals with a protonated methyl group (system 5, Table III) is always much greater than reaction of these species with a deuterated methyl group (system 2, Table III), and the reaction of these radicals with a protonated ring (system 3) is similarly greater than with a deuterated ring (system 4). Finally, both of the radicals react more with the toluene when it is protonated and the carrier is deuterium (system 1) than when the toluene is deuterated and the carrier is hydrogen (system 6).

The reactions of the phenyl radicals seem to depend less on whether or not the site is deuterated than does the methyl radical reactions, but in both cases the isotope effect seems almost to swamp out the differences in reactivity between ring and methyl group hydrogens. This behavior is characteristic of the reactions of methyl radicals with toluene, since Cher⁸ has shown that, at 60°, methyl radicals (from photolyzed azomethane) extract hydrogen (or deuterium) with equal probability from the ring or side chain of

toluene-d₈, but almost entirely from the side chain of toluene-d₆.

4. The data in Table II (or Table III) can be used to estimate the relative rates of phenyl or methyl reaction with protonated ring vs. reaction with protonated methyl group. The CD₃H/CD₄ ratio in runs 10, 11 divided by the CH₄/CH₃D ratio in runs 17 and 18 is 1.65; this is approximately⁹ equal to the rate constant ratio, k_{8rh}/k_{8sh} (where k_r or k_s refers to reaction with ring or methyl group, and h or d means hydrogen or deuterium extraction). A similar estimate of the rate constant ratio, $k_{7rh}/k_{7sh} = 3$, can be made for phenyl radicals. Evidently for both radicals reaction with the ring is preferred to reaction with the side chain at 750°. This is in contrast to the observations of Cher⁸ who found that the preferred reaction of methyl radicals at 60° was with the side chain. The difference observed here may reflect a change in mechanism between reactions at 60 and 750°, or it may reflect a change in the pre-exponential factor of the rate equation.

Finally some secondary conclusions can be reached. The importance of displacement-type reactions such as (3) and (4) is shown by the large amount of hydrogen–deuterium exchange in the toluene recovered from runs where deuterium was the carrier gas, and from the decreased deuterium content of deuterated toluenes recovered from runs where hydrogen was the carrier gas. The exchanges take place by analogous displacement processes. The conclusions reached here do not depend upon the amount of toluene conversion or deuterium exchange since the results of the runs here are qualitatively the same as the runs reported in the earlier paper.¹ The absence of xylenes or biphenyls in the reaction products of all the runs show that methyl or phenyl radicals do not substitute in the toluene ring under these conditions. This is in agreement with the observations of Cher,⁸ who found the methyl radicals (from photolyzed azomethane) do not add to toluene in the gas phase.

It is disturbing that somewhat less benzene than methane is produced in most of the runs made; this implies that some benzene is being consumed or methane made by processes other than those listed.

Finally a word may be said about the value of the hydrogen carrier technique for studying thermal decompositions, as described in this paper. The technique is useful if the thermally decomposing molecules form radicals which are stable enough to react with the hydrogen. Under these conditions, the number of pyrolysis products formed is reduced markedly, and analysis of the mechanism by isotope tracer techniques is profitable. Even when no apparent change in products results from use of hydrogen or deuterium carrier, as in the case of ethane,¹⁰ isotope scrambling which sometimes results can reveal unsuspected features of the mechanism.

On the other hand, use of carrier hydrogen with a flow system, as reported here is not always the best way in which to study the reactions of the radicals

(9) The actual full expression is

$$\frac{0.08/0.92}{0.05/0.95} = \frac{k_{8rh}}{k_{8sh}} \left[\frac{k_8(\text{Me})(\text{D}_2) + k_{8rd}(\text{Me})(\text{T}) + k_3(\text{D})(\text{T})}{k_8(\text{Me})(\text{D}_2) + k_{8sd}(\text{Me})(\text{T}) + k_3(\text{D})(\text{T})} \right]$$

where Me is methyl radical and T is toluene. The $k_8 + k_3$ terms are much larger than the k_8 terms so that the term in brackets is approximately equal to unity.

(10) J. G. Burr and J. D. Strong, unpublished data.

(7) A. Blades and E. W. R. Steacie, *Can. J. Chem.*, **32**, 1142 (1954).

(8) M. Cher, *J. Phys. Chem.*, **68**, 1316 (1964).

formed in the pyrolysis. A static system in which the ratio of hydrocarbon to hydrogen is more easily controlled is preferable for study of the radical reactions; such a study is under way in the toluene-hydrogen system.

Acknowledgment.—We want to acknowledge many helpful conversations with Mark Cher of this laboratory, and his help in working out many of the problems in kinetics.

[CONTRIBUTION FROM THE AEROSPACE CORPORATION, EL SEGUNDO, CALIF.]

The Photolysis and Pyrolysis of 4-Methyl-4-methoxy-2-pentanone^{1a}

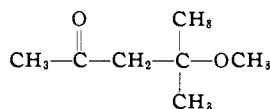
BY D. J. COYLE,^{1b} R. V. PETERSON, AND JULIAN HEICKLEN

RECEIVED JANUARY 13, 1964

The photolysis of 4-methyl-4-methoxy-2-pentanone yields mesityl oxide, methanol, and an hydroxyfuran derivative (compound F; see Results) as products. Small amounts of acetone and methyl isopropenyl ether are formed also. The ratios of products are not affected by the extent of conversion, the temperature, or the addition of oxygen, and are only slightly affected by altering the solvent. Thus, free-radical processes are eliminated, especially since both a product, mesityl oxide, and one of the solvents used, allyl alcohol, are good radical scavengers. The Norrish-Bamford type II dissociation would be expected to yield as products acetone, methyl isopropenyl ether, and a cyclic alcohol. The appropriate alcohol was not observed in our experiments, and the acetone and isopropenyl ether were only minor products. The furan derivative is a more important product and probably forms through a seven-member ring intermediate (see Discussion) which opens and then recloses to give the product. Mesityl oxide and methanol are formed in both photolysis and pyrolysis. In the photolysis, all of the radiation is absorbed. Since one of the products, mesityl oxide, also absorbs in the same region as the reactant, it inhibits the photolysis by removing some of the incident radiation. In the pyrolysis, no such inhibition takes place.

Introduction

In an effort to develop a knowledge of the chemical behavior of electronically excited carbonyl compounds, a difunctional ketone



containing structural features which could give rise to competitive reactions of the excited state, has been studied. It is well known that a ketone with a hydrogen-bearing carbon in the γ -position gives rise to a smaller ketone and an olefin.²⁻¹⁰ The results to 1957 were reviewed by Pitts.¹¹ At that time, it was not clear whether the intermediate involved a six-member ring containing the carbonyl group or a four-member ring excluding the carbonyl group. However, the later work of Srinivasan⁶ established beyond reasonable doubt the six-member intermediate. More recently, Ausloos and Rebbert¹² have shown that in addition to the β -cleavage of the ring, a cyclic alcohol can be formed, presumably also *via* the ring intermediate.

The compound photolyzed in this study has two γ -carbons bearing six hydrogen atoms. In another γ -position is a CH_3O group bearing three hydrogen atoms in the δ -position. If bond strengths exert a critical effect upon the course of the primary step, then the

activating effect of the oxygen atom might be able to exert a drastic modification on the course of the reactions.

Experimental

Starting Materials.—A commercial sample of 4-methyl-4-methoxy-2-pentanone (for simplicity, hereinafter referred to as Pentoxone, trademark of Shell Chemical Co.) was obtained and was purified by distillation at reduced pressure in a 2-ft. long, 8-mm. heligrad Podbielniak column. A cut was obtained with a 99.95% purity as determined by gas chromatographic analysis. The impurity present was identified as mesityl oxide. The purified material was stored in a brown glass bottle under argon pressure at 0°.

Pure grade heptane from Phillips Petroleum Co. was purified further by reacting with an aqueous potassium permanganate solution, washing with water, drying with CaCl_2 , and finally, distilling in a 20-plate bubble-cap column.

Eastman allyl alcohol was distilled in the above-mentioned heligrad column to a 99% purity.

Absolute ethanol was used as obtained from U. S. Industrial Chemical Co. A negligible amount of impurity was found with the gas chromatograph.

Preparation of Samples for Photolysis.—The liquid-phase photolysis samples were prepared by charging 7-mm. o.d. Vycor tubes of approximately 8-in. length with 2 ml. of the Pentoxone solution. The solutions were prepared by injecting 1 ml. of Pentoxone and 10 ml. of solvent into a serum-stoppered, argon-purged, brown glass bottle.

The solutions charged into the Vycor tubes were degassed to approximately 10^{-5} mm. and sealed, except for series III which was under 1 atm. O_2 pressure.

Photolysis Procedures.—Solution photolysis of the Pentoxone was accomplished with a Hanovia Type SOL 100-w. mercury lamp. The lamp was placed in a quartz tube with a water-cooling jacket, and this assembly was set up in a constant temperature ($\pm 1^\circ$) water bath. The Vycor tubes containing the solutions were placed in the water bath equidistant from the light source. The samples were irradiated with the full arc.

The irradiated tubes were either analyzed immediately or stored at -25° until analysis. In one experiment, the Vycor tubes were replaced with 13-mm. Pyrex tubes.

Product Analysis.—Analysis of the photolysis products was accomplished on the gas chromatograph (g.c.). Two g.c.'s were used: a Beckman GC-2A and an F & M Model 720.

The irradiated Pentoxone in solution was analyzed by immediately withdrawing 5 to 10 μl . of the solution into a syringe after breaking the top off the tube. Immediately, the photolyzed

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