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.


The Photolysis and Pyrolysis of 4-Methyl-4-methoxy-2-pentanone[1a]

BY D. J. COYLE,[1b] R. V. PETERSON, AND JULIAN HEICKLEN

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

$$CH_3—\overset{\overset{\displaystyle O}{\|}}{C}—CH_2—\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}—OCH_3$$
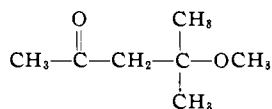
containing structural features which could give rise to competitive reactions of the excited state, has been studied. It is well known that a ketone with a hydrogen-bearing carbon in the γ-position gives rise to a smaller ketone and an olefin.[2-10] The results to 1957 were reviewed by Pitts.[11] At 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 Srinivasan[8] established beyond reasonable doubt the six-member intermediate. More recently, Ausloos and Rebbert[12] 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. heligrid 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 heligrid 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 (±1°) 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

(1) (a) The work reported here was completed at Aerospace Corp. Publication was supported by the U. S. Air Force under Contract No. AF 04(695)-269. (b) Deceased, July 14, 1963.

(2) (a) R. G. W. Norrish and M. E. S. Appleyard, *J. Chem. Soc.*, 874 (1934); (b) C. H. Bamford and R. G. W. Norrish, *ibid.*, 1538 (1938).

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(7) P. Ausloos and E. Murad, *ibid.*, **80**, 5929 (1958).

(8) R. Srinivasan, *ibid.*, **81**, 5061 (1959).

(9) P. Ausloos, *J. Phys. Chem.*, **65**, 1616 (1961).

(10) J. L. Michael and W. A. Noyes, Jr., *J. Am. Chem. Soc.*, **85**, 1027 (1963).

(11) J. N. Pitts, Jr., *J. Chem. Educ.*, **34**, 112 (1957).

(12) P. Ausloos and R. Rebbert, *J. Am. Chem. Soc.*, **83**, 4897 (1961).

material was injected into the liquid port of the gas chromatograph.

In earlier experiments a 16-ft. long, 0.25-in. o.d. column containing 40% 2R446 Resoflex on 45–60 mesh Chromosorb W was used in the g.c. analyses. A 10-ft. long, 0.25-in. o.d. column containing 15% Carbowax 20M on 60–80 mesh Diatoport P gave superior resolution and was used exclusively in later experiments.

The major product peaks in the gas chromatogram were identified by comparison of elution times with known materials, where possible.

The peak thought to be mesityl oxide was confirmed by trapping the material from a prep column 6 ft. long and 0.5 in. in diameter, and scanning the material in an infrared spectrophotometer. The infrared spectrum of the trapped material was identical with that of a known quantity of mesityl oxide.

Identification of the high boiling unknown compound began by trapping the material from the above-mentioned column fitted to the gas chromatograph. Samples of the high boiling unknown were run in the infrared and ultraviolet spectrophotometers, and the nuclear magnetic resonance and mass spectrometers. The unknown compound did not absorb above 2200 Å. in the ultraviolet region, and characteristic bands in the infrared showed up at 3450, 2900–3000, 1380, 1460, and 1050 cm.$^{-1}$. The first band is the OH stretching frequency. The last band is the most intense and is characteristic of the C–O–C group. The other bands correspond to CH_3 and CH_2 stretching and bending modes. The most prominent mass spectral peaks appeared at m/e 115, 85, 57, and 43. The peak at 31 corresponding to CH_3O^+ was not very large. The mass spectral data indicate that the parent mass is at least 115, that the CH_3O group is probably absent, and that CH_3 groups are present. The 43 peak which was the largest is suggestive of CH_3CO and this combination is almost certainly present. The nuclear magnetic resonance data were obtained and analyzed by Dr. A. G. Whittaker of the Aerospace Corp. He showed conclusively the absence of CH_3O, and the presence of $HOCCH_3$, CH_3CCH_3, $-CCH_2C-$, $-CH_2O-$, and $-OH$. A study of the composite instrumental analysis of the unknown material yielded the structure 2,2,4-trimethyl-4-hydroxy-3,5-dihydrofuran (F).

An elemental analysis yielded a carbon–hydrogen ratio of 0.48, whereas the calculated ratio for F is 0.50. A molecular weight determination was run on the unknown using the freezing point depression technique with benzene as a solvent. The results yielded a molecular weight of 133 in good agreement with that of 130 for F.

Quantitative analyses of the gas chromatograms were obtained by multiplying the area under the peak by the calibration factor for the material. The area under the peak was calculated by multiplying the height of the peak by the width at the half-height.

The calibration factors for the materials were obtained by determination of the area units per given mole fraction; a moles-per-area-unit factor thus was obtained. This was done for the starting material and all identified products except the methyl isopropenyl ether, for which the calibration factor was assumed to be the same as that for acetone.

Quantum Yield Determination.—The quantum yield of decomposition in a 12 weight % n-heptane solution was obtained by irradiating the solution at 3130 Å. and measuring the molecules converted.

A Hanovia 500-w. Type A mercury lamp, two 3-in. quartz converging lenses, an iris, and a filter passing 3175 ± 65 Å. were mounted on an optical bench. A 20-mm. diameter × 10-mm. path length quartz cell was positioned directly behind the filter.

The output of the lamp was measured by chemical actinometry using 0.01 M uranyl sulfate and 0.05 M oxalic acid.

The amount of Pentoxone converted was calculated by summing the product areas from the g.c. analysis.

Pyrolysis.—The gas-phase pyrolysis experiments were performed at 200° in 25-mm. Pyrex tubes fitted with a break seal and degassing stem. The volume of the tubes was approximately 40 ml.; 50 µl. of the purified Pentoxone (99.95%) was charged into the tubes. The material was then degassed to 10^{-5} mm., and the tube was sealed.

The degassed samples were placed in an oil bath regulated at 200 ± 0.5°. The products and remaining starting material from the pyrolysis were vacuum-transferred to a small, tapered

vial. The vial was removed from the vacuum line, and the products were analyzed immediately on the g.c. by injection with a microliter syringe.

The isomesityl oxide formed in the pyrolysis was identified by trapping from a g.c. and analyzing on the mass spectrometer and infrared spectrophotometer.

Results

Several series of runs were made under various conditions. The liquid was photolyzed in different media, at three temperatures, and in the presence and absence of oxygen. The Pentoxone was also pyrolyzed in the vapor phase at 200°. The results are presented in Tables I–III.

The products found from photolysis were methanol, mesityl oxide (MO), a hydroxyfuran derivative (F), acetone, and two other products with chromatograph retention times corresponding to low molecular weight ethers. One of these products is produced in amounts similar to acetone and is undoubtedly methyl isopropenyl ether (E). The other product is produced in very small quantities (less than 10% of the acetone) and was not identified. Unfortunately, the chromatograph retention time of the ethers was the same as for heptane; thus, analyses could not be made when heptane was the solvent.

mesityl oxide (MO)　　　　　　　　　　　F　　　　　　　　　　　E
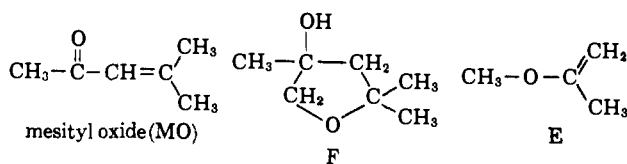
The principal results are: (a) Neither a change in temperature nor the presence of oxygen changes any of the results significantly. (b) The product ratios are not dependent on the percentage conversion. For some series, the methanol to mesityl oxide ratio appears to increase from a small value to unity as the conversion becomes larger. However, this is an artifact due to the probable loss of methanol by vaporization before analysis; this loss is most pronounced at low conversions. Simple mass balance considerations require the methanol to mesityl oxide ratio to be unity. The similar trend noted in some cases for the acetone to mesityl oxide ratio probably results from the same cause. It should not be unexpected that some loss of highly volatile materials, such as methanol and acetone, would occur. (c) Even though the total number of quanta absorbed is constant with time, the decomposition rate falls off markedly as exposure time increases. This diminution of rate increases in importance in the various media in the order: pure Pentoxone, heptane, ethanol, allyl alcohol. (d) The ratios acetone/MO and F/MO are somewhat larger in the two alcohol solvents than in pure Pentoxone or heptane. (e) The acetone to methyl isopropenyl ether ratio is close to unity in the two alcohol solvents in conformance with mass balance requirements. However, in pure Pentoxone, almost no ether was found. (f) Photolysis in Vycor tubes gives less than twice the amount of products as does photolysis in Pyrex tubes for the same exposure time. Thus, most of the photodecomposition results from excitation at 3130 Å. The results reported here are for Vycor tubes. (g) In heptane solutions, the

TABLE I

PHOTOLYSIS OF PENTOXONE (9.1 VOLUME %) IN HEPTANE

Time of run, hr.	Mole %					Methanol/MO	Acetone/MO	F/MO
	Pentoxone	Acetone	Methanol	MO	F			
Series I, $T = 25°$								
0.50	92.88	0.18	1.42	3.85	1.66	0.37	0.047	0.43
0.75	91.23	.36	2.00	4.70	1.71	.43	.077	.36
1.00	86.72	.56	3.83	5.86	3.03	.65	.096	.52
2.17	86.15	.69	2.94	7.16	3.05	.41	.097	.43
4.50	62.58	1.44	12.77	16.00	7.22	.80	.09	.45
6.08	58.74	1.80	13.62	17.87	7.97	.76	.10	.45
Series II, $T = 25°$								
2.00	75.22	0.94	7.95	11.53	4.36	0.69	0.081	·0.38
5.00	63.39	1.22	11.78	17.36	6.24	.68	.070	.36
7.75	48.66	2.00	18.70	21.37	9.28	.88	.093	.43
12.25	39.65	2.17	21.96	25.11	11.09	.88	.086	.44
21.00	37.12	2.41	22.69	25.97	11.80	.87	.093	.45
28.00	28.90	2.50	26.1	29.3	13.9	.89	.085	.47
50.00	16.46		32.73	34.05	16.75	.96	. . .	.49
Series III, $T = 25°$, solution saturated with O_2								
1.00	83.40	Trace	5.33	7.67	3.60	0.69	. . .	0.47
2.00	78.43	1.0	6.99	9.50	4.09	.74	0.105	.43
6.00	59.19	2.15	13.55	16.24	8.88	.83	.132	.55
8.72	52.99	2.27	16.30	19.22	9.22	.85	.118	.48
17.00	41.31	2.94	19.89	23.28	12.57	.85	.126	.54
29.72	27.97	3.5	23.15	29.55	16.21	.78	.118	.55
Series IV, $T = 45°$								
3.00	77.36	0.68	6.73	10.36	4.86	0.64	0.065	0.46
6.50	62.09	1.01	13.77	15.32	7.8	.9	.066	.51
12.00	53.07	1.59	16.21	18.54	10.59	.88	.086	.57
20.50	40.10	1.73	21.05	23.04	14.08	.91	.075	.61
29.00	27.12	2.59	27.21	26.27	16.81	1.03	.098	.64
Series V, $T = 75°$								
2.50	85.36	0.74	3.85	6.51	3.55	0.59	0.11	0.54
7.75	59.83	3.14	10.25	16.89	9.89	.61	.18	.58
19.25	43.53	5.61	17.98	21.08	11.80	.85	.27	.56
27.00	27.12	6.78	28.27	23.78	14.04	1.19	.28	.59

TABLE II

PHOTOLYSIS OF PENTOXONE AT 25° IN OTHER MEDIA

Time of run, hr.	Mole %						Methanol/MO	Acetone/MO	F/MO	E/MO
	Pentoxone	Acetone	Methanol	MO	F	E				
Series VI, pure pentoxone										
1.00	98.16	0.13	0.61	0.78	0.29	0.02	0.78	0.167	0.37	0.03
2.00	97.46	0.20	0.95	1.03	0.34	.02	0.91	.192	.33	.02
7.00	93.71	0.51	2.44	2.28	1.03	.02	1.07	.224	.40	.01
Series VII, 9.1 volume % pentoxone in ethanol										
2.00	87.53	1.11	2.81	8.81	3.43	1.30	0.74	0.29	0.90	0.34
6.00	75.00	2.87	6.25	4.50	8.30	3.07	1.39	.64	1.84	.69
10.00	66.64	2.89	11.75	9.4	7.19	2.12	1.25	.31	0.77	.23
21.00	49.60	3.94	16.74	13.83	11.60	4.26	1.21	.28	0.84	.31
Series VIII, 9.1 volume % pentoxone in allyl alcohol										
2.50	89.74	0.70	3.64	3.22	1.88	0.82	1.13	0.22	0.59	0.26
4.75	81.08	1.25	5.90	5.66	3.55	1.42	1.04	.22	.63	.25
16.00	67.20	2.19	11.56	10.15	6.75	2.23	1.12	.21	.61	.22
27.50	47.74	3.36	16.86	16.41	9.99	5.62	1.02	.20	.61	.34

limiting low conversion quantum yield of decomposition is about 0.46.

The pyrolysis results are listed in Table III. The major products are mesityl oxide and methanol. Smaller amounts of isomesityl oxide and acetone are formed also. Trace amounts (less than 5% of the acetone) of methyl isopropenyl ether and three other unidentified products were found. One of these products is the same as found for photolysis. The other two have chromatograph retention times cor-

responding to C_3- or C_4-hydrocarbons. As in the photolysis, the product ratios are unaffected by percentage conversion, except possibly that the relative importance of isomesityl oxide diminishes for larger conversions.

Discussion

The products of photolysis and their relative importance are unaffected by temperature, percentage conversion, or the presence of oxygen. Both oxygen

TABLE III

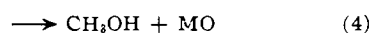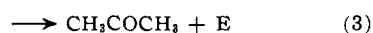GAS PHASE PYROLYSIS OF PENTOXONE AT 200°

| Time of run, hr. | Mole % | | | | | Methanol/MO | Acetone/MO | Iso-MO/MO |
	Pentoxone	Acetone	Methanol	MO	Iso-MO			
				Series IX				
1.00	95.31	0.08	2.00	2.16	0.45	0.93	0.04	0.21
2.00	94.65	.08	2.39	2.50	.39	.96	.03	.16
4.08	90.46	.11	4.36	4.54	.53	.96	.03	.12
6.50	66.58	.57	15.10	16.08	1.68	.94	.04	.105
16.00	40.58	.66	20.12	26.81	2.47	.75	.03	.092
24.00	22.34	1.36	32.41	39.80	4.09	.82	.04	.103
30.00	14.01	1.38	41.48	39.47	3.66	1.05	.03	.093
				Series X				
12.00	51.07	0.46	13.87	30.17	4.42	0.46	0.03	0.147
20.00	39.50	.81	30.26	26.61	2.82	1.13	.027	.106
24.00	28.64	.67	29.60	37.86	3.23	0.78	.023	.085
39.50	7.52	1.71	44.62	41.75	4.39	1.17	.038	.105

and mesityl oxide, one of the products, should be good radical scavengers. Furthermore, the solvent used does not change the products and only slightly alters their relative importance. This is of special significance since one series of runs was done with allyl alcohol, a powerful radical scavenger, as a solvent. These facts definitely establish that free radicals are not formed to any measurable extent.

Three primary processes are required to explain the photochemical results. The most important gives mesityl oxide and methanol. Another gives the hydroxyfuran derivative F, which is an isomer of Pentoxone. The third, and least important reaction produces acetone and methyl isopropenyl ether. Our failure to find sufficient methyl isopropenyl ether in the photolysis of pure Pentoxone or in the pyrolysis is difficult to understand. Either it or some other products with the same C/H/O ratio must be present.

The first primary process also takes place in the pyrolysis, whereas the furan-forming reaction does not. Thus, it seems reasonable to associate the furan production with the excited electronic state (which is absent in pyrolysis) and the mesityl oxide-forming process with either the upper electronic state or excited vibrational levels of the ground electronic state. The acetone-producing reaction might also occur from either electronic state. If the absence of E in the pyrolysis is significant, then its presence in photolysis supports the thesis that the excited electronic level is responsible for its formation in accordance with the Norrish–Bamford type II process.

The photochemistry can be explained by the mechanism

$$P + h\nu \longrightarrow P^* \tag{1}$$

$$P^* \longrightarrow F \tag{2}$$

$$\longrightarrow CH_3COCH_3 + E \tag{3}$$

$$\longrightarrow CH_3OH + MO \tag{4}$$

$$\longrightarrow P \tag{5}$$

where P represents Pentoxone, P* represents electronically excited Pentoxone. Steps 3 and 4 might involve excited vibrational levels of the ground electronic state as an intermediate. The quantum yield estimate indicates that about 17% of P* gives the furan, about 4% goes to acetone and E, about 25% gives mesityl oxide and methanol, and the remaining 54% deactivates. These values are for the heptane solutions but are not markedly different in the other media.

It is of interest to speculate on the details of the primary steps. The most reasonable way of forming the furan is through an intermediate involving a seven-member ring
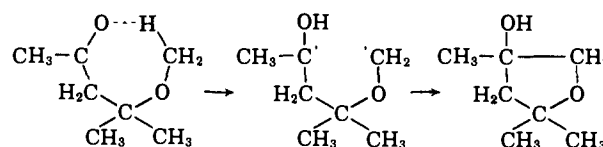

The type II process, involving one of the γ-hydrogens in a six-member ring, predicts the formation of acetone and methyl isopropenyl ether and a cyclobutanol (B)
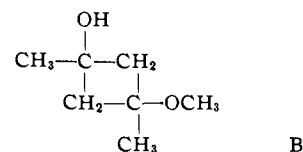

Acetone and methyl isopropenyl ether were found, but the cyclobutanol B was not. It cannot be established whether acetone and E are produced from the upper electronic state via a type II process or via another process. However, these products are much less important than the furan. Thus, even though there are twice as many γ-hydrogens as methoxy hydrogens, the seven-member ring is preferentially formed to the six-member ring, perhaps because the methoxy hydrogens are more labile.

The formation of mesityl oxide and methanol probably occurs in a four-center reaction
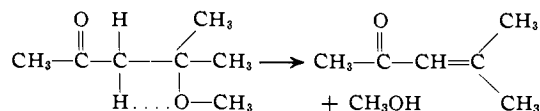
Dr. H. Takimoto of Aerospace Corp. has suggested to us the possibility that the reaction could involve the enol form of the ketone and thus proceed via a six-member ring structure
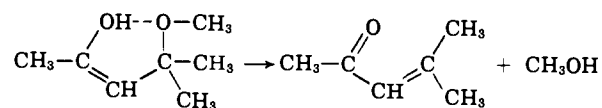
At 200° (i.e., in the pyrolysis) some of the mesityl oxide presumably isomerizes, thus giving rise to isomesityl oxide.
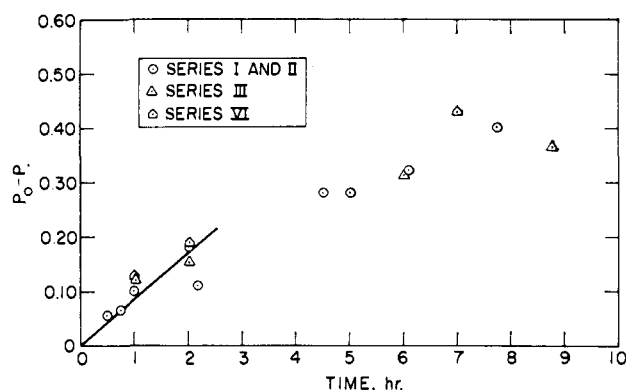
Fig. 1.—Plot of $P_0 - P$ vs. time of photolysis.

Since all the radiation incident on the sample is absorbed, the rate of pentoxone removal should be constant during irradiation. Figure 1 is a plot of the change in concentration (P_0-P) vs. time of exposure for series I, II, III, and VI. The four series all fit the same plot, and for small times the plot is linear. At longer times, the data lie far below the linear extension of the curve, thus demonstrating that the products inhibit decomposition. The other series were not plotted because results are not available at times short enough to fit the linear portion. However, the higher temperature data (series IV, V) correspond to the plot. The data for the ethanol and allyl alcohol solutions show much greater inhibition, and it is not clear whether the initial rate of decay would be the same as for the other series.

One of the products is mesityl oxide which absorbs radiation in the 3200 Å. region. The radiation absorbed by mesityl oxide is not available to photodecompose the pentoxone, thus giving rise to the observed inhibition.

Since the mesityl oxide absorbs radiation, it also might photodecompose. This possibility was checked by photolyzing mesityl oxide in heptane solutions. The mesityl oxide is remarkably stable; the only product found was a trace of acetone, even after an extended photolysis. This might partially explain the relative increase of acetone observed in the Pentoxone photolysis as irradiation proceeded.

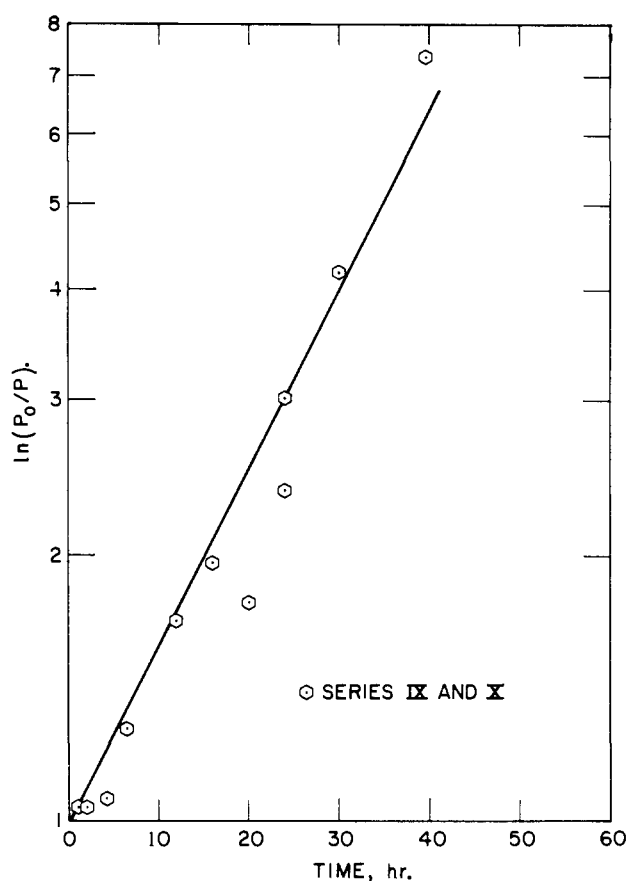The pyrolysis results give a check to see if the in-

Fig. 2.—Plot of ln (P_0/P) vs. time for pyrolysis of Pentoxone.

hibition is really due to absorption by the mesityl oxide. Since there is no radiation, the decomposition should be uninhibited and follow first-order kinetics

$$\ln (P_0/P) = kt \qquad (6)$$

where k is the unimolecular rate constant at 200° Figure 2 is a plot of ln (P_0/P) vs. t. The scatter is bad, but the plot shows no indication of inhibition with reaction time. The rate constant k is about 0.045 hr.$^{-1}$.

Acknowledgment.—The authors wish to thank Mr. Anthony Leonardi-Cattolica for useful discussions and Mrs. Barbara Peer for assistance with the manuscript.

[Contribution from·Department of Applied Chemistry, Faculty of Engineering, Nagoya University, Nagoya, Japan]

Kinetics of the Autoxidation of Phenylhydroxylamines to Azoxybenzenes in Methanol

By Yoshiro Ogata, Yasuhiko Sawaki, Jiro Mibae, and Takashi Morimoto

The autoxidation of phenylhydroxylamines in methanol has been studied kinetically by estimating consumed oxygen. The rate is proportional to the product of the concentration of phenylhydroxylamine and the partial pressure of oxygen and is not affected by the addition of radical initiators or inhibitors, but is accelerated by a basic catalyst, methoxide ion. A mechanism was postulated which involves one-electron transfer to oxygen molecule from both free phenylhydroxylamine and its conjugate base, but not from the conjugate acid of phenylhydroxylamine. The substituent effect in pure methanol satisfied the Hammett's law to give a ρ-value of -1.56.

Phenylhydroxylamine in aqueous solution is easily oxidized by oxygen to nitrosobenzene and hydrogen

$$2C_6H_5NHOH + O_2 \longrightarrow$$

$$C_6H_5NO{=}NC_6H_5 + H_2O_2 + H_2O \quad (1)$$
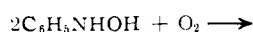
peroxide, and the nitrosobenzene formed condenses rapidly with phenylhydroxylamine to produce azoxybenzene.[1]

(1) E. Bamberger, Chem. Ber., 27, 1550 (1894); 33, 113 (1900).