

[CONTRIBUTION FROM THE NATIONAL BUREAU OF STANDARDS, WASHINGTON 25, D. C.]

The Photolysis of Ethyl Vinyl Ether

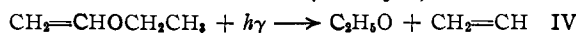
BY E. MURAD^{1,2}

RECEIVED AUGUST 10, 1960

The photolysis of ethyl vinyl ether has been studied with and without mercury photosensitization. In both cases the primary processes were



An additional primary process was found to occur in the Co^{60} - γ -radiolysis, *viz.*



The configuration of the excited state leading to process II is suggested to be a six-membered ring.

Introduction

The photolysis of ethyl vinyl ether was undertaken to ascertain whether there is a photochemical process analogous to its thermal decomposition in which ethylene and acetaldehyde are formed in a direct unimolecular process.³ Interest in the present investigation was, therefore, centered on the non-free radical decomposition of the ether, although the free radical decomposition is also discussed.

Experimental

Reagents. Ethyl Vinyl Ether.—Ethyl vinyl ether, practical grade, from Distillation Products, Industries, was fractionally distilled.⁴ The final product was 99.1% pure as indicated by gas chromatography. The impurities were 0.70% diethyl ether and 0.15% acetaldehyde. It was believed that this small concentration of acetaldehyde would not interfere with the mechanism of the photochemical decomposition of the ether.

Oxygen.—Assayed reagent-grade oxygen was obtained from The Matheson Co.

Nitric Oxide.—Nitric oxide from The Matheson Co. was purified by distilling the sample from a trap at -160° to a trap at -195° and then outgassing the latter material at -215° . Mass spectrometric analysis of the nitric oxide thus purified showed no impurities.

Carbon Dioxide.—Assayed reagent-grade carbon dioxide was obtained from The Matheson Co.

Apparatus and Procedure.—A Hanovia S-100 medium pressure mercury arc was used in all the direct photolysis experiments. The light was focused by means of a quartz lens onto a quartz cell, 10 cm. in length and 5 cm. in diameter. No filters were used, since ethers do not absorb appreciably at wave lengths longer than 2000 Å. In experiments on the mercury photosensitized decomposition a low pressure spiral mercury arc was used. The principal wave length was 2537 Å. A conventional type vacuum apparatus was used. The volume of the cell system was 534 ml. A sample was condensed into the cell system and thoroughly outgassed before photolysis. In oxygen-ether and in nitric oxide-ether experiments, efficient mixing was accomplished by means of a mercury expansion bulb. Conversions were of the order of 0.5%.

After photolysis the products were condensed at -112° and then distilled through two traps, one at -195° and the other at -215° (solid nitrogen). In experiments in which oxygen was added to the ether, the non-condensable gases were pumped off, while in experiments in which oxygen was not added, the noncondensable gases were collected in a Toepler pump and measured. This fraction contained CO , CH_4 and H_2 . It was oxidized over CuO at 260° , where CO

and H_2 were oxidized to CO_2 and H_2O . Methane and CO_2 were separated at -195 and -78° and subsequently measured. Hydrogen was determined by difference. The purity of CO_2 was always checked on the mass spectrometer (Consolidated Model 21-620). The analysis for hydrogen was checked by analyzing with a sensitive mass spectrometer (Consolidated Model 21-103) the non-condensable gases from a similar experiment.

The condensable residue from the other traps was then transferred to a LeRoy still,⁵ and from this the ethane-ethylene fraction was removed at -173° and analyzed with the mass spectrometer. In experiments without added oxygen, the residue in the LeRoy still was collected in a sample tube behind a break seal and analyzed on a Perkin-Elmer Vapor Fractometer, Model 154. A Perkin-Elmer Column L at 0° was used to analyze this fraction, which contained butane, acetaldehyde and the parent compound. It also contained some CO_2 , present in the starting material, which could not be removed by distillation. In experiments with added oxygen this last fraction was discarded.

Results

Quantum yields were not determined in the present work. Therefore, only rates of formation are reported. All experiments were performed at room temperature, about 26° .

A series of experiments was made in which a constant amount of oxygen and a varying amount of the ether was taken. In these experiments only ethylene was determined. The data are given in Table I.

In Table II are shown the results of: (a) direct photolysis of the ether in the absence of oxygen; (b) a mercury-photosensitized decomposition of the ether; (c) two experiments in which the γ -radiolysis of the ether was conducted in the presence and in the absence of oxygen.

An attempt was made to study the photolysis of ethyl vinyl ether in the presence of iodine, but this proved futile due to the reaction of iodine with the ether.

Table III gives the results of another series of experiments in which the ether was photolyzed in the presence of other gases. In these experiments another lot of the parent compound was used. In addition, the optical system for this series was also different, although the dimensions were the same. As a result, the intensity was 0.14 that of the previous experiments. In this series the non-condensable fraction was not always analyzed, since the primary interest was in the amount of ethylene and acetaldehyde.

(1) National Research Council, National Bureau of Standards, Postdoctoral Research Associate, 1959-1960.

(2) Department of Chemistry, University of Wisconsin, Madison 6, Wis.

(3) A. T. Blades and G. W. Murphy, *THIS JOURNAL*, **74**, 1039 (1952).

(4) The distillation was kindly performed by Dr. R. T. Leslie of these Laboratories.

(5) D. J. LeRoy, *Can. J. Chem.*, **B28**, 492 (1950).

TABLE I

PHOTOLYSIS OF ETHYL VINYL ETHER IN THE PRESENCE OF OXYGEN

Partial pressure of O₂ = 9 mm., temp. = 27°, length of photolysis = 400 sec., and volume of cell system = 534 ml.

Pressure of ether (mm.)	11	25	75	101	102	101 ^a	204	370
Rate of formation of C ₂ H ₄ (mole × 10 ⁹ /sec.)	2.30	2.22	2.04	1.80	1.79	0.02	1.68	1.44

^a A Corning filter No. 7380, which cuts off all radiation below 2100 Å., was used in this experiment.

TABLE II

PHOTOLYSIS OF PURE ETHYL VINYL ETHER

Temp. = 27°; volume of cell system = 534 ml.

Pressure of ether (mm.)	30	24.5 ^b	52.5 ^c	103	27	25 ^d	102 ^e	102 ^f
Length of photolysis (sec.)	40	400	400	400	3600	400	14,400	14,400
Relative incident intensity	1	1	1	1	1/12	1	<i>a</i>	<i>a</i>
Rate of formation of product (mole × 10 ⁹ /sec.)								
CO	0.85	1.54	1.51	1.34	0.17	0.91	4.1 × 10 ⁻²	<i>a</i>
CH ₄	0.05	0.09	0.14	0.12	.009	<i>a</i>	0.2 × 10 ⁻²	<i>a</i>
H ₂	0.20	0.16	0.05	0.08	.014	0.14	0.7 × 10 ⁻²	<i>a</i>
C ₂ H ₄	2.20	2.44	2.21	2.49	.23	3.68	7.7 × 10 ⁻²	7.9 × 10 ⁻²
C ₂ H ₆	0.30	0.35	0.36	0.50	.03	0.65	0.6 × 10 ⁻²	0.0
C ₄ H ₁₀	<i>a</i>	3.04	3.36	0.51	.21	4.79	1.52 × 10 ⁻²	0.0
CH ₃ CHO	<i>a</i>	1.50	3.71	4.51	.32	1.55	9.7 × 10 ⁻²	<i>a</i>

^a Product was not determined. ^b Rates are averages of 3 runs. ^c Rates are averages of 2 runs. ^d Hg-sensitized, 2537 Å. ^e Radiolysis in absence of oxygen; also present was some 1-C₄H₈, rate = 1.47 × 10⁻¹¹ mole/sec. ^f Radiolysis in presence of oxygen.

TABLE III

PHOTOLYSIS OF ETHYL VINYL ETHER IN PRESENCE OF ADDED GASES

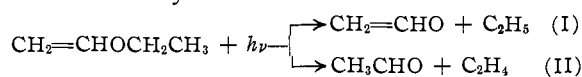
Temp. = 25°; volume of cell system = 534 ml.

Pressure of ether (mm.)	13.5	25.0	25.9	26.0 ^o
Added gas	None	None	CO ₂	NO
Pressure of added gas (mm.)	26.0	1.0
Length of photolysis (sec.)	1620	3000	3000	3000
Rate of formation of product (mole × 10 ¹⁰ /sec.)				
CO	<i>a</i>	1.65	<i>a</i>	6.16
CH ₄	<i>a</i>	0.20	<i>a</i>	0.14
H ₂	<i>a</i>	<i>c</i>	<i>a</i>	<i>c</i>
C ₂ H ₄	2.59	2.65	2.19	1.59
C ₂ H ₆	0.83	0.97	0.61	0.0
C ₄ H ₁₀	3.85	4.56	4.73	0.0
CH ₃ CHO	1.98	2.16	1.96	1.70

^a Product was not determined. ^b In this experiment some nitrogen was produced, undoubtedly due to the decomposition of nitric oxide. The rate of formation of nitrogen was approximately 1.0 × 10⁻¹⁰ moles/sec. ^c The height of the mass spectrometric peak at *m/e* = 2 in the absence of nitric oxide approximately the same as in the presence of nitric oxide.

Discussion

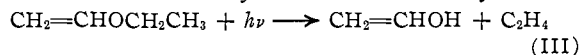
Primary Processes.—Two primary processes which certainly occur are



The absence of 1-butene and 1,4-butadiene indicates that a primary process to give vinyl radicals and ethoxy radicals does not occur in the photolysis. The presence of *n*-butane is evidence for primary process I. The production of ethylene in abundant quantities in the presence of oxygen

(Table I) and nitric oxide (Table III) indicates that a major part of the ethylene is formed in a direct molecular process. Acetaldehyde was not determined in experiments with oxygen present, since the oxidation of ethyl radicals would be expected to give acetaldehyde. However, the addition of nitric oxide did not affect the rate of production of acetaldehyde, from which fact it may be concluded that acetaldehyde arises from a direct molecular process the same process, in fact, that gives rise to ethylene.

In the photolysis of diethyl ether^{6,7} a primary process giving ethyl alcohol and ethylene was suggested. A similar process in ethyl vinyl ether would lead to vinyl alcohol and ethylene, *viz.*



However, vinyl alcohol is unstable in its monomeric form and rearranges to acetaldehyde.^{8,9} Even if this process were to occur, it would be indistinguishable from process II, since the end product would be the same.¹⁰ In view of these remarks

(6) A. J. Harrison and J. S. Lake, *J. Phys. Chem.*, **63**, 1489 (1959).

(7) To confirm the occurrence of this process under the present experimental conditions, the mercury-sensitized decomposition of diethyl ether was studied in the presence of oxygen. At an ether pressure of 57 mm. and an oxygen pressure of 4 mm., about one-fifth as much ethylene was produced as in a similar experiment with ethyl vinyl ether. This result agrees with conclusions of Harrison and Lake.

(8) See G. W. Wheland, "Advances in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1949, pp. 89-90.

(9) See also F. C. Whitmore, "Organic Chemistry," D. Van Nostrand Co., Inc., New York, N. Y., 1951, pp. 133-135.

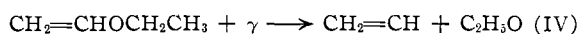
(10) The author wishes to thank one of the referees for pointing out that the enol form of acetaldehyde (*i.e.*, vinyl alcohol), if formed, will not rearrange immediately but might have long enough lifetime to diffuse to the wall, and, perhaps, undergo some reactions (*cf.* R. Srinivasan, *THIS JOURNAL*, **81**, 5061 (1959)). That most of the vinyl alcohol rearranges to acetaldehyde is shown by the data of Table III. In this Table, if 0.10 *R*C₄H₁₀ is subtracted from *R*C₂H₄ (to correct for the disproportionation of the ethyl radicals),¹¹ the remainder in *R*C₂H₄ agrees with *R*CH₃CHO.

(11) The ratio of disproportionation to recombination of ethyl radicals is 0.10. See A. F. Trotman-Dickenson, "Gas Kinetics," Butterworths Scientific Publications, London, 1955, p. 236.

it is pointless to consider process III any further, since under the conditions of these experiments, its products cannot be differentiated from the products of process II. The data of Table II show that at a pressure of ethyl vinyl ether of 24.5 mm. ethylene exceeds acetaldehyde, even after correcting for the disproportionation of ethyl radicals. It is hard to explain this result and it may be due to experimental error. The increase in the rate of formation of acetaldehyde with increasing pressure will be considered in a later section.^{12,13}

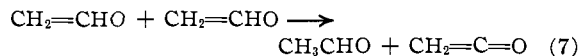
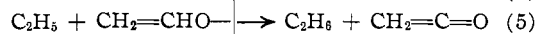
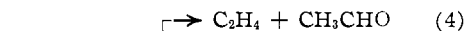
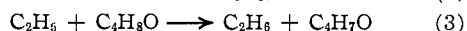
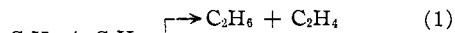
An approximate estimate indicates that at least 75–80% of the photochemical decomposition proceeds *via* process I (depending on the mechanism of formation of ethane).¹⁴

Two experiments were performed in which ethyl vinyl ether was irradiated with γ -rays from Co⁶⁰. The results indicate that both processes I and II occur in the radiolysis also. It is not possible to estimate the extent of process I, since at high pressures of ethyl vinyl ether ethyl radicals add to the ether (see below). One surprising aspect of the radiolysis of this ether is the formation of 1-butene, which indicates the occurrence of the reaction



No butadiene was found in this experiment.

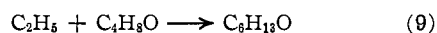
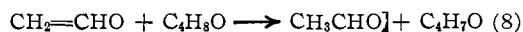
Free Radical Reactions.—Free radical reactions which may occur in this system are



(12) It may be remarked that the ratio of the rate of formation of acetaldehyde to the rate of formation of ethylene seems to increase sharply when the pressure of ethyl vinyl ether is increased from 24.5 mm. to 50 mm. as shown by the data of Table II. Aside from the possibility of an experimental error, it might seem that extrapolation to zero pressure still shows that $\text{CH}_3\text{CHO}/\text{C}_2\text{H}_4$ tends towards zero. However, although direct comparison may not be made between the data of Table II and Table III, the latter shows that the ratio of $\text{CH}_3\text{CHO}/\text{C}_2\text{H}_4$ does not change upon going from 13 to 25 mm., the percentage decomposition being the same.

(13) A comparison of the decrease in the rate of production of ethylene in the photolysis of the ether in the presence of oxygen (Table I) with that of the pure ether (Table III) shows that this decrease is not very large. The results of Table III indicate that nitric oxide is considerably more effective in decreasing this rate. However, these results should be considered with some caution, since nitric oxide undergoes some photochemical decomposition under the conditions of these experiments (as shown by the production of nitrogen in the photolysis). Oxygen atoms are known to react very rapidly with ethylene at room temperature.

(14) The total decomposition may be taken to be $(2[\text{C}_4\text{H}_{10}] + 0.10[\text{C}_4\text{H}_8] + [\text{C}_2\text{H}_4])$, where the brackets indicate amounts of products. Decomposition due to process I is: $\{2[\text{C}_4\text{H}_{10}] + 0.20[\text{C}_4\text{H}_8]\} / (2[\text{C}_4\text{H}_{10}] + 0.10[\text{C}_4\text{H}_8] + [\text{C}_2\text{H}_4])$. Such calculations were carried out for the runs where the pressures were below 100 mm., and the results for Table II indicate an average of 75%, while those of Table III indicate an average of 82%. These estimates are lower limits, since the following assumptions were made: (1) no ethane arises from sources other than disproportionation of ethyl radicals; (2) the recombination of ethyl and vinyloxy radicals was not considered; (3) the addition of ethyl radicals to the double bond in ethyl vinyl ether was likewise not considered.



$\text{C}_4\text{H}_8\text{O}$ in the above equations represents ethyl vinyl ether. Reactions 4, 7 and 8 may also be written so that the tautomer of acetaldehyde (vinyl alcohol) is first produced, followed by the rearrangement of vinyl alcohol to acetaldehyde. The above equations will now be discussed in terms of the observed products.

A. At low pressures ethane and butane are formed by reactions 1 and 2, respectively. At low pressures the ratio of ethane to butane is what might be expected for reactions of two ethyl radicals.¹¹

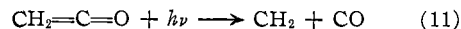
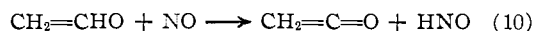
B. The sharp decrease in butane at high pressures of ethyl vinyl ether may be attributed to the addition of ethyl radicals to the double bond of the ether, *i.e.* reaction 9. Ethane is still formed at high pressures, which might indicate that at these pressures reaction 3 becomes an important source of ethane.

C. The increase in the rate of formation of acetaldehyde with increasing pressure is due to reaction 8.¹⁵ No conclusion is possible about the extent of reaction 4 as a source of acetaldehyde.

D. The mechanism of formation of CO and CH_4 is not clear. One possibility is the rearrangement of the vinyloxy radical to acetyl radical and the subsequent decomposition of the acetyl radical to CO and CH_3 , the latter being the source of the methane. One objection to this suggestion is that the vinyloxy radical is resonance stabilized, *viz.*



E. The increase in the yield of CO in the presence of nitric oxide is interesting and may be due to the following sequence of reactions

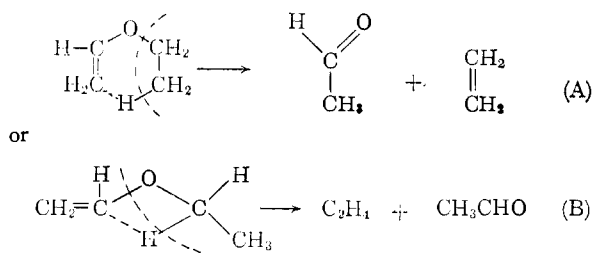


Reaction 11 is quite plausible as a source of CO, since ketene absorbs at wave lengths longer than 3000 Å., where the intensity of the Hanovia S-100 lamp is quite high.

F. The mechanism of formation of hydrogen is not clear. Since nitric oxide did not remove or appreciably reduce the rate of formation of hydrogen, it may be that it is formed in a primary process which yields H_2 in one step.

Configuration of the Excited State Leading to Process II.—Blades and Murphy³ first postulated process II in their study of the thermal decomposition of ethyl vinyl ether. While in that study they were unable to establish whether the intermediate reactant was a six-membered or a four-membered ring, *viz.*

(15) Such a suggestion is not implausible since recent work indicates that abstraction of hydrogen atoms by alkoxy radicals proceeds with low activation energies. See, for example, M. H. J. Wijnen, *THIS JOURNAL*, **82**, 3034 (1960).



Blades¹⁶ in a later study of the thermal decomposition of vinyl isopropyl ether suggested that (A) is the correct configuration, since the products were acetaldehyde and propylene. Configuration (A)

(16) A. T. Blades, *Can. J. Chem.*, **31**, 418 (1953).

must also be the process leading to photodecomposition according to process II, since the photolysis of methyl vinyl ether does not yield ethylene, while the photolysis of *n*-butyl vinyl ether yields butene and acetaldehyde.¹⁷

In conclusion it may be mentioned that the effect of pressure on the rate of formation of ethylene in the presence of oxygen (Table I) seems to imply an excited state which may be deactivated by collisions. The scatter, however, does not allow an unambiguous decision.

Acknowledgment.—The author wishes to thank Dr. P. Ausloos for his advice and encouragement during the progress of this work.

(17) E. Murad, unpublished results.

[CONTRIBUTION FROM WASHINGTON UNIVERSITY, SAINT LOUIS, MISSOURI]

Association Between Sodium and Naphthalenide Ions¹

BY N. M. ATHERTON AND S. I. WEISSMAN

RECEIVED OCTOBER 10, 1960

The electron spin resonance spectrum of the naphthalene negative ion in dimethoxyethane has been observed under very high resolution and improved values of the hyperfine coupling constants evaluated. It has been established that the more complex spectrum of the sodium derivative observed in tetrahydrofuran solution can be attributed to interaction with the sodium nucleus of spin 3/2. The sodium splitting is observed to be temperature dependent, and the existence of an ion-ion pair equilibrium is demonstrated. Sodium splittings were also measured in 2-methyltetrahydrofuran, tetrahydropyran and dioxane. Suggestions are made concerning a possible structure of the ion pair and the mechanism yielding spin density at the sodium nucleus.

Introduction

Over the past few years the electron spin resonance (e.s.r.) spectra of the negative ions of many aromatic compounds, formed by reaction of the compound with an alkali metal in a dry ether-type solvent, have been studied by several groups of workers. One of the most extensively studied radicals has been the naphthalene negative ion, and the interpretation of the spectrum is well established.^{2,3} The hyperfine pattern arises from interaction with the two sets of four equivalent protons, and of the 25 lines expected for such a system 17 have hitherto been resolved. The assignment of the lines was completed by measurements on α - and β -deuterated derivatives and the larger splitting shown to arise from nuclei in the α -position.^{2,3} This relatively simple pattern was obtained from the sodium, potassium and rubidium derivatives in dimethoxyethane (DME) solution and for the lithium and potassium derivatives in tetrahydrofuran (THF), but the spectrum from the sodium derivative in THF was anomalous, containing more lines than predicted for interaction with 8 protons, and the anomaly was not explained.⁴ An anomalous spectrum also was

reported for the sodium derivative in 2-methyltetrahydrofuran (Me-THF).

Recent improvements in spectrometer resolving power have made it possible to resolve all 25 lines in the "normal" spectrum and to re-measure the coupling constants. This improvement also suggested that some insight might be gained into the anomalous spectrum shown by the sodium derivative in THF and the present communication describes the results of this investigation and some analogous effects found in other solvents.

Experimental

The purification and storage of materials followed the lines already well established⁵ and the usual procedure for preparing the radical solutions was used. Absolute concentrations of radicals were determined using 1 cm. cells in a Cary recording spectrophotometer and a value of 2.20×10^3 for the extinction coefficient at 8000 Å.⁶ E.s.r. spectra were taken on a spectrometer designed by Professor J. Townsend of the Physics Department of this University. Low temperatures were achieved by boiling liquid nitrogen and streaming the cold gas past the sample tubes which were housed in a vacuum-jacketed quartz tube in the microwave cavity. The temperature was controlled by adjusting the boiling rate and, measured by a copper-constantan thermocouple, could be held constant to 1° over periods longer than that required to record a single spectrum.

Results and Discussion

Hyperfine Couplings in the Naphthalene Negative Ion.—In DME solution the sodium derivative

(1) This work has been supported in part by the U. S. Air Force under Contract and in part by an equipment loan contract with ONR. Acknowledgment is also made to the donors of the Petroleum Research Fund administered by the American Chemical Society for partial support of this research.

(2) S. I. Weissman, T. R. Tuttle and E. de Boer, *J. Phys. Chem.*, **61**, 28 (1957).

(3) T. R. Tuttle, R. L. Ward and S. I. Weissman, *J. Chem. Phys.*, **5**, 189 (1956).

(4) T. R. Tuttle, Ph.D. Thesis, Washington University, 1957.

(5) D. E. Paul, D. Lipkin and S. I. Weissman, *J. Am. Chem. Soc.*, **78**, 116 (1956).

(6) D. E. Paul, Ph.D. Thesis, Washington University, 1957.