

Addition of a small amount (2% molar) of dimethyl tetrasulfide to the trisulfide did not accelerate the rate of decomposition of the latter. This indicates that the following reaction does not occur at any appreciable rate.



A similar conclusion follows from consideration of the influence of azobisisobutyronitrile on the decomposition of dimethyl trisulfide. The initial rate of formation of dimethyl tetrasulfide is slightly accelerated, whereas the rate of production of disulfide is unaffected. It is almost certain that the role of the azobisisobutyronitrile is to generate isobutyronitrile radicals which subsequently attack the trisulfide. The following reactions are possible.



Reaction 8 may be excluded since the formation of $\text{MeS}\cdot$ radicals would almost certainly result in the production of dimethyl disulfide. For the same reason, the $\text{MeS}_2\cdot$ radicals produced cannot participate in reaction 7 but must undergo recombination to give dimethyl tetrasulfide.

These last two experiments show that the decomposition of dimethyl trisulfide does not occur by a free-radical chain reaction initiated by the fragments of homolytic dissociation. A nonchain radical mechanism is possible and the similarity in the rates of decomposition in the solvents benzene and nitrobenzene is in accordance with this mechanism. However, we feel that our evidence is not sufficient to allow a firm conclusion to be made at the present time.

Preliminary studies in our laboratories have indicated that polysulfenyl radicals, $\text{RS}_x\cdot$, where $x > 1$, have substantially different reactivity than sulfenyl radicals, $\text{RS}\cdot$.¹⁷ In the past workers have found that non-Markovnikov addition of sulfenyl radicals to olefins is suppressed in the presence of sulfur and polysulfides.^{2,3} Such results have been explained in terms of an ionic addition caused by the presence of sulfur. While such explanations are quite reasonable, we suggest that they be viewed with due caution until the reactions of polysulfenyl radicals are more completely understood.

Acknowledgments. The authors gratefully wish to acknowledge support from the Army Research Office (Durham) and to the Sulfur Institute, Washington, D. C.

(17) S. Chubachi, Ph.D. Thesis, Princeton University, 1966.

The Vacuum Ultraviolet Photochemistry of *o*-Xylene

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Abstract: The vapor-phase photolysis of *o*-xylene has been investigated using light of 1600–2100 Å. With the exception of a small amount of benzocyclobutene which is formed by vacuum ultraviolet photolysis, the same products are formed as those produced by irradiation with 2537-Å light (toluene, *m*-xylene, *p*-xylene, and *o*-ethyltoluene). This coincidence of products suggests that both photolyses may proceed through a common set of reactive intermediates. Fluorescence measurements, as well as the effect of added inert gases on the reaction, indicate that the first excited singlet and lowest lying triplet states are not suitable choices for such common intermediates. The intermediacy of highly vibrationally excited ground electronic states seems to be most consistent with the available facts. The mechanism of formation of benzocyclobutene has been investigated by deuterium labeling, and found to proceed by the loss of a single hydrogen (or deuterium) atom from each methyl group, rather than loss of molecular hydrogen from one methyl group. The construction of lamps which emit 10^{16} to 10^{17} quanta/sec in the vacuum ultraviolet is described.

The interest in the photochemical reactions of simple, noncondensed, aromatic hydrocarbons has recently been heightened by the reports of Wilzbach and Kaplan¹ of rearrangements to the nonbenzenoid "isomers" under irradiation at the 2537-Å mercury line. In the cases where the benzene ring is heavily substituted with bulky groups (*e.g.*, 1,2,4-tri-*t*-butylbenzene) these isomers are isolable;¹ with smaller groups the intermediacy of the isomers is inferred from the isomerization of labeled compounds.² These reactions occur with low quantum efficiencies, typically about 0.01.

(1) K. E. Wilzbach and L. Kaplan, *J. Am. Chem. Soc.*, **87**, 4004 (1965).

(2) (a) L. Kaplan, K. E. Wilzbach, W. G. Brown, and S. S. Yang, *ibid.*, **87**, 675 (1965); (b) K. E. Wilzbach and L. Kaplan, *ibid.*, **86**, 2307 (1964).

Irradiation with light of wavelengths of less than 2000 Å is expected to bring about reactions much more efficiently. This expectation is based on a report³ that no fluorescence was observed when simple aromatics (benzene, toluene, *p*-xylene, and mesitylene) were irradiated in the vapor phase at wavelengths corresponding to their second and third absorption bands, approximately 1600–2100 Å. It is reasonable that the failure to observe light emission may result from an efficient predissociation path available to the excited molecule.

Since only fragmentary reports of the vacuum ultraviolet photochemistry of aromatics were available, an

(3) C. L. Braun, S. Kato, and S. Lipsky, *J. Chem. Phys.*, **39**, 1645 (1963).

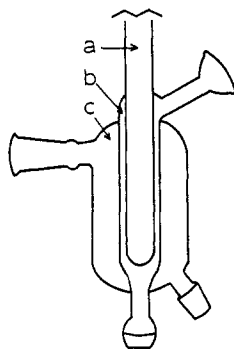


Figure 1. Vacuum ultraviolet discharge lamp: a, discharge tube; b, cooling jacket; c, photolysis cell.

investigation of the photolysis of very simple members of this compound class has been initiated in this laboratory. This paper is a report of the results observed from a single compound, *o*-xylene, and of the construction of light sources suitable for such an investigation.

Results

Vacuum Ultraviolet Light Sources. The most obvious practical reason for the neglect of studies of vacuum ultraviolet photochemistry has been the difficulty of the construction of sources of suitable intensity and stability. The production of very pure fused silica (Suprasil or Spectrosil) has been of great assistance in the solution of such problems. Lamps constructed of this material transmit light down to about 1600 Å and do not appear to degrade with use (as does lithium fluoride). Also, such lamps are relatively sturdy, and the organic polymers that are frequently deposited during photolyses are easily removed from them.

Two lamp designs were used in the present investigation; both were constructed of Suprasil where vacuum ultraviolet light transmission was required, and of ordinary fused silica elsewhere. Both lamps consisted of a discharge tube surrounded by a toroidal cell. One lamp was filled with xenon at a pressure of 190 torr as suggested by Wilkinson and Tanaka,⁴ and powered by a 2450-mc microwave generator. The discharge was contained in a Suprasil tube, part of which was surrounded by a quartz jacket which formed the photolysis cell; the unjacketed portion of the tube was inserted into a slotted wave-guide termination of the generator. The output of the lamp was inspected with a vacuum monochromator, and it agreed well with the published data.⁴ The principal ultraviolet output is a continuum which rises steeply from the Suprasil cutoff at 1600 Å to a maximum at 1760 Å and tails off to 2200 Å. No other radiation is observed until a few weak bands begin at about 3000 Å. The output of the lamp was about 6×10^{15} quanta/sec as measured by oxygen actinometry. The inner wall of the cell compartment was heated by the discharge to about 300°.

The second lamp design interposed a cooling jacket between the discharge and the photolysis cell (see Figure 1). The cell temperature was controlled by electrically heating the outer jacket and forcing nitrogen from a liquid nitrogen boiler through the inner cooling jacket. This lamp was filled with oxygen at 0.3–0.6 torr, and was powered in the same manner as the xenon

(4) P. G. Wilkinson and Y. Tanaka, *J. Opt. Soc. Am.*, **45**, 344 (1955).

lamp. The principal light output was a series of sharp lines beginning at 1600 Å⁵ and falling off to 2200 Å, with no further radiation at increasing wavelengths until a few weak and widely spaced lines appeared at 2800 Å. Approximately 95% of the ultraviolet light output below 2800 Å is between 1600 and 2000 Å. Intensity by oxygen actinometry was 10^{16} to 10^{17} quanta/sec, depending on the power input to the lamp. Temperatures in the cell could be varied from below 0 to 280°. The oxygen discharge appears to offer significant advantages over the xenon discharge in intensity, reproducibility, and cost. Since no particular care was used to purify the oxygen it is probable that impurities are present in the discharge, and there is some evidence that they are necessary to maintain the discharge.⁶

Photolysis with Vacuum Ultraviolet Radiation. The products obtained in the vacuum ultraviolet vapor-phase photolysis of *o*-xylene are listed in Table I. These products were formed in approximately the same ratios by both the xenon and oxygen lamps described above; the reported distributions are for photolysis with the oxygen lamp. The conversions in all photolyses were kept to less than 1% (and more usually <0.3%) to ensure that effectively all of the radiation was absorbed by the reactant. Thus direct photolytic destruction of products was prevented. Further reactions of products, photosensitized by *o*-xylene molecules, is of course not eliminated by this precaution.

Table I. Products of the Vapor-Phase Photolysis of *o*-Xylene^a

	Vacuum ultraviolet, ^d		2537 Å		<i>e</i>
	Static	Flow	25°	40°	
Benzene	2	<i>b</i>	<i>b</i>	<i>b</i>	0.6
Toluene	30	6	6	16	15.6
Ethylbenzene	3	<i>b</i>	<i>b</i>	<i>b</i>	0.5
<i>m</i> -Xylene	39	88	82	64	68.4
<i>p</i> -Xylene	5	5	10	7	6.2
Benzocyclobutene	5	2	<i>c</i>	<i>c</i>	<i>c</i>
<i>o</i> -Ethyltoluene	15	<i>b</i>	2	10	7.3
<i>m</i> -Ethyltoluene	1	<i>b</i>	<i>b</i>	2	1.4

^a The data are in mole %, normalized to 100% for the products reported. ^b Product present in minor amounts, less than 1 mole %. ^c Product could not be detected, <0.01 mole %. ^d The reported percentages are averages of analyses of three photolyses; the agreement was usually to $\pm 1\%$ or better between the individual photolyses. ^e Calculated from data reported by Wilzbach and Kaplan.^{2b}

Photolyses were carried out in both static and flow systems. The pressure of reactant in the photolysis cell in the static system was controlled by thermostating a reservoir of liquid *o*-xylene connected to the cell at 25°. The equilibrium vapor pressure is sufficiently high at this temperature to ensure that more than 99% of the incident light was absorbed by the sample.⁷

(5) The Suprasil cutoff at 1600 Å prevents photoionization of *o*-xylene, which does not set in until wavelengths of less than 1500 Å are reached.

(6) Lamps worked best with oxygen flowing past the discharge tube during the operation. Sealed lamps frequently failed after several-hours use, and one acceptable explanation is that "impurities" necessary for breakdown were destroyed during the first hours of operation.

(7) Calculated from the absorption spectra published by J. R. Platt and H. B. Klevens, *Chem. Rev.*, **41**, 301 (1947).

In the flow photolyses the *o*-xylene sample was carried through the cell in a helium stream at a total pressure of 1 atm. The concentration of *o*-xylene in the helium was monitored by a thermal conductivity cell and the products and unreacted *o*-xylene were trapped from the stream in a trap cooled with liquid nitrogen. The same products were formed in both systems, but the ratios were changed appreciably and the quantum yield for product formation (Φ , defined as quantum yield of formation for C₆ to C₉ compounds) was lower in the flow system ($\Phi = 0.10$) than in the static system ($\Phi = 0.17$).

Relatively large increases of the temperatures of the sample (from 150 to 240°) for photolyses in the flow system caused little change in product composition, but some increase in quantum yield: $\Phi = 0.02$ at 150° and $\Phi = 0.1$ at 240°. This increase in Φ is at least partially (and perhaps completely) due to the diminished formation of polymer on the lamp jacket at the higher temperature.

Mass spectral analysis of the noncondensable gas (at 77°K) present after a static photolysis indicated that hydrogen was present along with smaller amounts of methane. Polymer formation was visible only when the lamp was cooled (to about 150° or lower) or when large amounts of material were passed through the lamp in the flow system. The visible polymer at low lamp temperatures probably resulted from further photolysis of "dimeric" products which condensed on the "cold" lamp jacket. Some dimeric products are formed in amounts much smaller than the volatile products. The principal dimeric product has been identified by retention time as *o,o'*-dimethylbibenzyl; other compounds of similar molecular weight are present but have not been identified.

Polymer is certainly formed in photolyses at higher temperatures, because a slight decrease in light output of the lamp (about 10%) is observed by oxygen actinometry following a photolysis.⁸ Some ring fragmentation products, C₆ and less, were also formed in small amounts (less than 1 mole %), but could not be reproducibly measured and are not included in the reported quantum yields.

Photolysis at 2537 Å. The photochemistry of *o*-xylene at 2537 Å has been reported by Wilzbach and Kaplan.^{2b} Their results and those obtained under similar conditions (static system, 7 torr *o*-xylene pressure, 40°, low-pressure mercury lamp) in this study are in excellent agreement. When the experiment was repeated using a sample heated to 250° the product ratio changed only slightly.

Pyrolysis. To ensure that the products formed in photolysis at 250° were not merely pyrolytic products, some simple pyrolysis experiments were carried out. When *o*-xylene was passed through a quartz tube at 250° in a helium stream, no observable reaction occurred. At 580° a very small conversion was observed to products expected from free-radical reactions: benzene, toluene, *o*-ethyltoluene, and *o,o'*-dimethylbibenzyl. No benzocyclobutene or *m*- or *p*-xylene was formed.

(8) Quantum yields for polymer formation were not determined quantitatively because a photolysis to 1% conversion on samples of 50 mg did not give sufficient material for even approximate gravimetric determinations. Photolysis to much higher conversions or on larger quantities of material gave polymer coatings on the lamp windows which made Φ_{polymer} determinations inaccurate.

Discussion

The most striking feature of the results reported in Table I is the close correspondence between the products formed by irradiation at 2537 Å and with vacuum ultraviolet radiation. Except for the benzocyclobutene which is formed only in the vacuum ultraviolet photolysis, all of the appreciable products (greater than 1 mole %) formed at 2537 Å are also formed by the vacuum ultraviolet. It is possible that this similarity is merely coincidental and that excitation at these different energies leads to the same products by different paths; no data are in hand which exclude this possibility. However, an entirely reasonable alternative is that both photolytic systems lead to a common set of reactive intermediates which proceed to the stable products. Of the two hypotheses, the second is best supported by the product studies, and leads to interesting speculation as to the possible identities of such intermediates.

A summary of the facts which are relevant to such a speculation is presented below. These facts have been gathered from the results of the closely related photolysis of benzene,⁹ and from fluorescence studies in the vacuum ultraviolet³ as well as from the data reported in this study.

1. Fluorescence measurements³ with benzene, toluene, and *p*-xylene (vapor phase) clearly indicate that excitation in the first allowed absorption band ($\lambda < 2000$ Å) does not lead to light emission. It has been concluded from this study that neither the first excited singlet state (S₁) or the lowest triplet state can be formed by such irradiation. Similar studies have not been done for *o*-xylene, but the spectral assignments,⁷ absorption intensities,⁷ and photochemistry¹⁰ are so similar for *o*- and *p*-xylene that the assumption that S₁ and the lowest triplet are not formed by vacuum ultraviolet photolysis is a satisfactory one.

2. The addition of inert gases or an increase in reactant pressure decreases the observed quantum yield of benzene disappearance at 1849 Å¹¹ and a similar effect of inert gas is observed on the 2537-Å isomerization of *m*-xylene.^{2b} Helium (1 atm) lowered the Φ from *o*-xylene by 40%.

3. When oxygen is added to photolysis samples, it is found to be only slightly more effective in lowering conversions than are other foreign gases. Thus oxygen was only three times as effective in quenching *m*-xylene isomerization as was nitrogen (both at 100 torr, *m*-xylene at 5–7 torr).^{2b} Oxygen (2 torr) had no effect on the disappearance of benzene (1 torr) with 1849-Å irradiation.¹¹

4. Pyrolysis of *o*-xylene at 550° led to a few of the photolysis products in very low conversions, but the major product, *m*-xylene, was not formed.

5. Product ratios from both 2537 Å and the vacuum ultraviolet photolysis of *o*-xylene were changed by changes in temperature and by addition of inert gases.

(9) There is every reason to believe from spectral assignments⁷ that the same excited states are being examined in each case. Photoproducts are very different in the two cases because the principal reactions which occur with the xylenes are either reiterative (isomerization) or impossible (loss of methyl or benzylic hydrogen) with benzene. As a result no photoproducts form from benzene with 2537-Å radiation in the vapor phase [J. N. Pitts, Jr., J. K. Foote, and J. K. S. Wan, *Photochem. Photobiol.*, **4**, 323 (1965)], and the principal reaction with vacuum ultraviolet irradiation is the formation of fulvene [H. R. Ward, J. S. Wishnok, and P. D. Sherman, Jr., *J. Am. Chem. Soc.*, **89**, 162 (1967)].

(10) H. R. Ward, unpublished data.

(11) K. Shindo and S. Lipsky, *J. Chem. Phys.*, **45**, 2292 (1966).

The excited state which *prima facie* is expected to be common between excitation at 2537 Å and by the vacuum ultraviolet is the S_1 state, since intersystem crossing from higher singlets to the first excited singlet is usually thought to be very efficient.¹²

The S_1 state seems unlikely as a common reactive intermediate in this case for several reasons. First, fluorescence studies³ (1) strongly suggest that this state cannot be formed by vacuum ultraviolet irradiation. Second, inert gas gives almost no quenching of benzene fluorescence¹³ (when pressures in the range of these experiments are considered), but does quench *m*-xylene isomerization.^{2b} Finally, oxygen has no effect on benzene disappearance at 1849 Å (3) even though it is known to quench the S_1 state.¹¹ The presence of any triplet state in the reaction scheme also can be eliminated by the small effect of added oxygen.¹⁴

A higher singlet, S_n , can hardly be reached by 2537-Å excitation, but can be eliminated as an intermediate leading directly to products even from vacuum ultraviolet photolysis, because its lifetime is so short (10^{-12} sec) that no effect of added inert gas would be expected³ (collision times under these conditions are about 10^{-9} to 10^{-10} sec). The most reasonable remaining alternatives for common reactive intermediates are various highly vibrationally excited ground electronic states (S_0^*). Thus a molecule excited to an S_n state might undergo rapid internal conversion to such a S_0^* state; conversion from S_1 to S_0^* must compete with fluorescence. The higher quantum yield for product formation with the vacuum ultraviolet than with 2537 Å is consonant with such a system.

The effect of oxygen in decreasing the quantum yield of isomerization of *m*-xylene may be due to quenching of S_1 before internal conversion occurs. Added inert gases would be expected to decrease Φ of product formation by collisional deactivation. This postulate is also consistent with the observations listed in I. Similar arguments have been used by Shindo and Lipsky¹¹ to propose an excited ground state in benzene photolysis.

The sensitivity of product ratios to changes in temperature and added foreign gases indicates that the products do not proceed directly from any single excited state. A single intermediate which could lead to such a variety of products would be very difficult to visualize in any case. It is not possible from the available data to say anything about which vibrational states might be involved, but a close inspection of the product ratios reported in Table I leads to some interesting suggestions. Thus at constant temperature, introduction of 1 atm of helium (in the vacuum ultraviolet system) causes a decrease in Φ which is almost entirely in products involving bond cleavage and bond formation (called, for convenience, decomposition products). Isomerization proceeds almost unhindered. This is consistent with a model in which highly vibrationally excited molecules lead to isomeriza-

tion in a time comparable to collisional times and other vibrational states (probably lower lying than those leading to isomerization) lead less rapidly to decomposition. Although energy surfaces are so complex as to be almost abstract for molecules as complicated as *o*-xylene, this situation is approximated by a surface leading to isomerization which crosses the ground-state surface at a high vibrational level, and a surface which crosses at a lower level leading to decomposition products. Reactions which lead to isomerization probably give the initially formed isomer at a high vibrational level. An increase in sample or foreign gas pressure should operate to stabilize the isomer and prevent its further decomposition. This expected effect is also compatible with the observed results.

Such a model is also consistent with the effect of temperature on product distribution in 2537-Å radiation. Internal conversion from the S_1 level would probably enter the ground-state manifold at a level lower than that for S_n crossing. Raising the sample temperature would give a greater number of molecules the vibrational energy necessary to isomerize. Such a model predicts that hot-tube pyrolysis should lead mostly to decomposition, since the vibrational levels are populated from the bottom in a Boltzmann fashion and excited molecules would be "siphoned" off onto the decomposition route before gaining enough energy to isomerize. The conceptual model is of course highly oversimplified. It is probably more reasonable to postulate that each decomposition product results from different levels of vibrational excitation. Also, if the simple model were to be strictly applied, it would predict a larger relative percentage of isomerization in vacuum ultraviolet photolysis than is actually observed.

Wilzbach and Kaplan found no evidence of *p*-xylene at low photolytic conversions of *o*-xylene vapor.^{2a} In vacuum ultraviolet photolysis, *p*-xylene is present even at conversions of 0.05%, and in a relatively constant ratio with *m*-xylene, so that it is most unlikely that *p*-xylene forms from a further isomerization of *m*-xylene. The suggestion of Wilzbach and Kaplan that isomerization proceeds through intermediates of benzvalene (I) and prismane types (II) has considerable



experimental support. A benzvalene intermediate formed from *o*-xylene can lead only to *m*-xylene (or back to *o*-xylene), all three isomers can be formed from the dimethylprismanes. (No stable dimethylbenzvalene or dimethylprismane has yet been detected in this system.) The suggestion of Bryce-Smith and Longuet-Higgins¹⁵ that the first excited singlet state in benzene should lead to benzvalene, and the lowest triplet to prismane appears to be inapplicable to *o*-xylene at least (*vide supra*). The exact method by which isomerization occurs has not been established for the xylenes, nor has the excited state leading to isomerization been identified. Hopefully these problems will yield to experiments presently in progress.

Mechanism of Benzocyclobutene Formation. The only isolated product that is unique to the vacuum

(12) N. Turro, "Molecular Photochemistry," W. A. Benjamin, Inc., New York, N. Y., 1965, p 64.

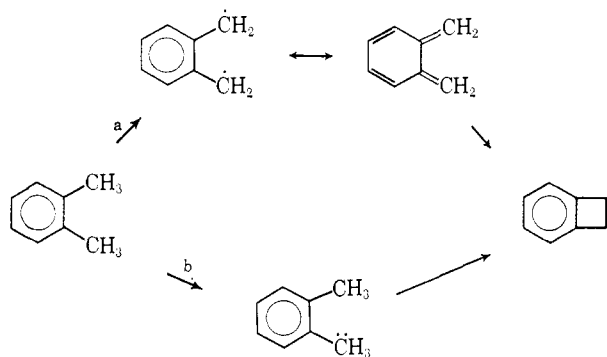
(13) H. Ishikawa and W. A. Noyes, Jr., *J. Chem. Phys.*, **37**, 583 (1962); G. B. Kistiakowsky and C. S. Parmenter, *ibid.*, **42**, 2942 (1965).

(14) Oxygen is reported to bring about the radiationless quenching of both excited singlets and triplets on virtually every collision (J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," John Wiley and Sons, Inc., New York, N. Y., 1966, p 599).

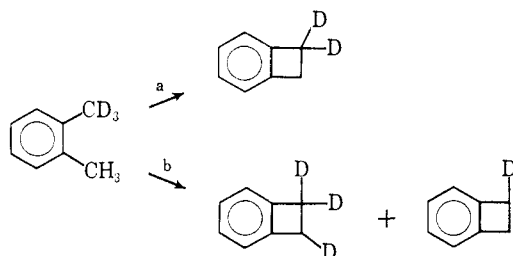
(15) D. Bryce-Smith and H. C. Longuet-Higgins, *Chem. Commun.*, 593 (1966).

ultraviolet photolysis of *o*-xylene (as compared to 2537 Å) is benzocyclobutene. This product must also result from some vibrationally excited and relatively long-lived intermediate because its yield is decreased by both a decrease in temperature and by an increase in foreign gas pressure.

To effect the formation of benzocyclobutene, two hydrogen atoms must be lost from the *o*-xylene molecule, most probably from the methyl groups. Two routes can be envisioned for this loss.



Both routes can be supported by analogy to known photochemical reactions. Cleavage of C-H bonds to form benzylic radicals (as in a) has been demonstrated by Porter and Wright.¹⁶ Loss of molecular hydrogen from a single carbon atom (as in b) is the preferred mode of decomposition of ethane with 1470-Å photolysis.¹⁷ The proof that benzocyclobutene is predominantly formed by path a was obtained by the photolysis of α,α,α -trideuterio-*o*-xylene. The isotopic content of the benzocyclobutene product was deter-



mined by mass spectroscopy at low ionizing voltage. A gas chromatograph direct coupled to a mass spectrometer showed that 90% of the benzocyclobutene contained two deuterium atoms, and only 4% d_3 and 5% d_1 . This particular analysis provides a convincing demonstration of the power of this analytical combination. The photolysis was run on a 35-mg sample of the deuterated material, and the product contained about 3 μ g of benzocyclobutene. This amount of material would have been sufficient to obtain over 100 satisfactory analyses of product distribution (from the gas chromatograph trace) and isotopic composition (from the mass spectrometer output).

Experimental Section

Vacuum Ultraviolet Lamps. Xenon Lamps. Research grade xenon (at 190 torr) was sealed in a Suprasil tube, 12 mm o.d. \times 14 cm, and 9 cm of the length was enclosed in a 20-mm o.d. quartz jacket which was fitted with ground joints at the top and bottom.

The lamp was powered by inserting the unjacketed stub of the Suprasil envelope into the slotted wave guide of a PGM-100 Raytheon microwave power generator (2450 mc, 150-800 w). The lamp was cooled during operation by air blasts from several directions.

Oxygen Lamps. The lower 8-cm portion of a 12 mm o.d. \times 16 cm Suprasil tube (0.5-mm wall) was jacketed by a 18 mm o.d. Suprasil tube carrying ground joints at the bottom and near the top ring seal. This jacket was used for cooling the lamp. The cooling jacket was in turn enclosed by a 40-mm o.d. quartz jacket, also fitted with top and bottom joints, which comprised the photolysis cell (see Figure 1). The discharge tube of this lamp was not sealed, but operated with oxygen flowing past the top of the discharge tube through a T joint. The pressure was held at 0.3-0.6 torr (as measured by a thermocouple gauge) by an adjustment of a needle valve on an oxygen cylinder leading to the T joint and a needle valve leading away from the T joint to a mechanical pump. The lamp was powered in the same manner as the xenon lamp. The light output was inspected by a Robin, 0.5-m vacuum monochromator through the top joint of the photolysis cell.

Actinometry. Oxygen actinometry was used to measure the output of both lamps. Oxygen was passed through the photolysis cell at 100-160 cc/min and bubbled through a dispersion tube into a 0.1 M solution of potassium iodide buffered with sodium acetate and acetic acid. The I_3^- concentration was determined spectroscopically at 350 $m\mu$. Duplicate determinations usually agreed to $\pm 5\%$.

Photolysis Technique. Static System. The *o*-xylene sample (Phillips Petroleum Research grade) was placed in a small flask on the bottom joint of the cell of the oxygen lamp, frozen at 77°, the jacket was evacuated to 0.005 torr, and the sample was degassed by a freeze-thaw cycle. The cell was isolated by a stopcock and the sample flask thermostated at 25°. After allowing sufficient time for equilibrium to be reached, the lamp was started, and cooling nitrogen was passed through the cooling jacket. The extent of cooling was determined by the voltage on a heater in a liquid nitrogen boiler. After the photolysis, the sample was condensed in the flask and removed for analysis.

Flow Systems. The *o*-xylene sample was injected into a glass container installed in the place of a column in the oven of an Auto-prep gas chromatograph. The effluent stream from the thermal conductivity cell was conducted to the photolysis cell through a heated line. The temperature of the *o*-xylene was controlled by the oven thermostat, the helium flow was held constant by the chromatograph flow controller, and the *o*-xylene concentration was precisely monitored by the chromatograph detector. For sample sizes of 0.1 ml at temperatures of 40 to 50° the technique gave a nearly constant *o*-xylene concentration for greater than 90% of the photolysis time. Samples were trapped at liquid nitrogen temperature for analysis.

Photolysis at 2537 Å. Ten germicidal lamps (GE G25-T8) were arranged in a 26-cm diameter circle with a stainless steel reflector surrounding the lamps. The photolysis cell was a fused quartz tube, 2.54 cm o.d. \times 54 cm, fitted with a sample holder and a stopcock. The sample of *o*-xylene (0.01 ml) was frozen in the sample holder, the cell was evacuated to less than 0.005 torr and isolated with the stopcock, and the sample was allowed to warm to room temperature. The cell was suspended along the vertical axis of the circle of lamps during the photolysis. For photolysis at 250°, the cell was loosely wrapped with fine resistance wire. Temperatures inside the tube were measured by a thermocouple. Heating by this method showed a variation of $\pm 10^\circ$ along the tube; the reported temperature is an average.

Pyrolysis. A quartz tube 1.8 cm o.d. \times 14 cm was wrapped with resistance wire for use as a pyrolysis tube. The *o*-xylene sample was passed through the tube in a helium stream, as described for the vacuum ultraviolet photolysis flow system.

Analysis. All analyses were done by flame-ionization gas chromatography, occasionally in conjunction with mass spectroscopy. The most useful columns were 5% DEGA-5% Bentone-34 on 100-120 mesh Chromosorb W, $\frac{1}{8}$ in. o.d. \times 20 ft, operated at about 70°. A support-coated Carbowax 1540 capillary column, 0.02 in. i.d. \times 50 ft, was useful in separating benzocyclobutene from the ethyltoluenes. Analysis for dimeric hydrocarbons was done on Silicone SE-30, Silicone QF-1, and DEGA-Bentone-34 columns at higher temperatures (100-140°). Quantitative determinations were averages of triplicate analyses, and areas were measured by planimeter or disk integrator and corrected for sensitivity to the flame detector to give the mole fraction. Identification was by comparison of retention times with known compounds on at least two (and

(16) G. Porter and F. Wright, *Trans. Faraday Soc.*, **51**, 1469 (1955).

(17) R. F. Hampson, Jr., J. R. McNesby, H. Akimoto, and I. Tanaka, *J. Chem. Phys.*, **40**, 1099 (1964).

usually three) columns, and by comparing the fragmentation pattern in the mass spectrum. In the gas chromatograph-mass spectrometer combination, a Varian Aerograph, Model 204-2, was connected by a low volume heated line, fed through an effluent stream splitter, to the helium concentrator of a Perkin-Elmer-Hitachi RMU 6-D.

Synthesis of α,α,α -Trideuterio-*o*-xylene. A solution of 2.65 g (0.0175 mole) of methyl *o*-toluate and 0.6 g of lithium aluminum deuteride (Metal Hydrides) in 10 ml of ethyl ether was stirred at reflux for 12 hr. Work-up with aqueous acid gave 2.14 g (0.0172 mole) of a white solid, mp 31–33° (lit.¹⁸ *o*-methylbenzyl alcohol mp 34°). The crude dideuterio alcohol (1 g) was added to 20 ml of cold, freshly distilled thionyl chloride, and the solution was slowly warmed to the boiling point and refluxed until gas evolution ceased. Excess thionyl chloride was removed on a rotary evaporator, and small portions of pentane were added and removed under vacuum to flush out the remaining traces of thionyl chloride. The resulting clear oil was dissolved in 20 ml of dry tetrahydrofuran and stirred

(18) "Handbook of Chemistry and Physics," 32nd ed, Chemical Rubber Publishing Co., Cleveland, Ohio, 1950, p 806.

at reflux under nitrogen with 0.26 g of lithium aluminum deuteride. The reaction mixture was acidified, and the product *o*-xylene was extracted into a known volume of pentane. Comparison of the gas chromatogram of this solution with a standard mixture indicated that 0.76 g of the deuterated *o*-xylene was present (theory, 0.88 g). The *o*-xylene was isolated by preparative gas chromatography to ensure purity of the sample. Analysis by mass spectroscopy at reduced ionization voltage showed the *o*-xylene to be 98% d_3 and 2% d_2 , with no detectable amounts of d_1 or d_0 .

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Photochemistry of Sodium 9-Anthroate in Aqueous Solution¹

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Abstract: The photochemistry of sodium 9-anthroate in aqueous solution has been investigated. Earlier reports that irradiation of sodium 9-anthroate in the presence of air gives photodimer and anthraquinone have been confirmed, and carbon monoxide, 10,10'-bianthrone, and anthracene have also been isolated. In degassed solutions sodium 9-anthroate gives anthrol anion and carbon monoxide. Air oxidation of the anthrol anion is responsible for formation of anthraquinone and 10,10'-bianthrone. The photochemical isomerization of sodium 9-anthroate to anthrol anion is considered to be analogous to the photoisomerization of 9-nitroanthracene.

Recent investigations of vinyl^{2,3} and aryl^{2,4} nitro compounds have uncovered photochemical rearrangements in which the nitro group isomerizes to a nitrite ester which then gives rise to products.

Irradiation ($\lambda < 410 \text{ m}\mu$) of 9-nitroanthracene gives, for example, 10,10'-bianthrone as the major product and lesser amounts of anthraquinone and anthraquinone monooxime,^{2,5} while β -methyl- β -nitrostyrene gives 1-phenyl-1-oximino-2-propanone.^{2,3}

As one aspect of our investigation of these rearrangements, we have considered whether the carboxylate anion which is isoelectronic with the nitro group might show related rearrangements. Both the nitro group and the carboxylate group are capable of $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions. Sodium 9-anthroate was selected for initial study because of its relationship to 9-nitroanthracene. Weigert and Ludwig have reported⁶ that irradiation of aqueous solutions of sodium 9-anthroate which were open to air gave a precipitate (anthraquinone)

(1) Photochemical Transformations, part XVIII. Portions of this report were abstracted from the M.S. thesis of A. W. Bradshaw, Iowa State University of Science and Technology, 1966.

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(6) F. Weigert and L. Ludwig, *Ber.*, **47**, 898 (1914).

