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The Mechanism of the Formation of Nonisomeric Products in the Vapor Phase Vacuum Ultraviolet Photolysis of *o*-Xylene

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Abstract: The mechanism of the formation of toluene, *o*-ethyltoluene, and other nonisomeric products in the vacuum ultraviolet photolysis of *o*-xylene has been investigated. Isotopic distribution in the products of the photolysis of an equimolar mixture of *o*-xylene-d_0 and *o*-xylene-d_6 indicates the mechanism to be radical in nature. These data plus the data from the photolysis of *o*-xylene-d_6 and from the photolysis of *o*-xylene-d_0 in the presence of deuterium gas indicate the primary process to be the homolytic cleavage of a benzylic carbon–hydrogen (deuterium) bond. The hydrogen atoms resulting from this process add to the aromatic ring of an *o*-xylene molecule giving toluene and methyl radicals. These methyl radicals react in part by combining with xylyl (methylbenzyl) radicals produced in the primary process to yield *o*-ethyltoluene. The rate of loss of α-hydrogen atoms from *o*-xylene-d_0 was determined to be 2.5 times as great as the rate of loss of α-deuterium from *o*-xylene-d_6. The hydrogen atoms produced in the primary process react as "hot" atoms.

The vacuum ultraviolet photolysis of *o*-xylene is known to result in the formation of toluene, *o*-ethyltoluene, 2,2′-dimethylbibenzyl (xylyl dimer), and other nonisomeric products in addition to the isomeric *p*- and *m*-xylenes.[2] These nonisomeric products can be thought of as arising by either of two mechanistic pathways. The first is the homolytic cleavage of C–H and/or C–C bonds resulting in radicals which could add, abstract, or recombine in many imaginable ways to give the observed products. The other reasonable mechanistic pathway is the loss of a methylene group from the xylene to yield toluene directly. Methylene could insert in the benzylic carbon–hydrogen bond of another xylene molecule to give *o*-ethyltoluene. In pyrolysis and ordinary (near ultraviolet) photolysis, this second possibility is generally ignored because of the large energy requirement of such a process. In the vacuum ultraviolet photolysis, this possibility should be considered because of the very large amount of energy available. One einstein of 1800-Å light gives 159 kcal of energy. The vacuum ultraviolet photolysis of ethane at 1470 Å is believed to result, in part, in the loss of methylene.[3]

$$C_2H_6^* \longrightarrow CH_2 + CH_4$$

Results

Mixtures of *o*-xylene-d_0 and *o*-xylene-d_6 (fully methyl deuterated) were photolyzed with light from an oxygen discharge using a reactor that has been previously described.[2a] The ultraviolet output of this reactor is a series of closely spaced lines in the 1600–2000-Å region.[4] Using cool nitrogen gas in the buffer zone of the reactor, the temperature during photolysis was kept to about 30°. The mixtures were made approximately equimolar. When a mixture deviated by more than 1% from equimolarity,[5] the results were corrected to equimolarity to facilitate comparisons. The results

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[1] National Science Foundation Graduate Trainee, 1965–1968.

[2] (a) H. R. Ward, *J. Amer. Chem. Soc.*, **89**, 2367 (1967). (b) The products are, with one exception, the same as in the 2537-Å photolysis: K. E. Wilzbach and L. Kaplan, *ibid.*, **86**, 2307 (1964).

[3] H. Okabe and J. R. McNesby, *J. Chem. Phys.*, **34**, 668 (1961).

[4] More than 95% of output of the lamp below 2800 Å is in this region.

[5] The *o*-xylene-d_5 in the mixtures was considered as *o*-xylene-d_6 when determining the molarity of the components of the mixture. An equimolar mixture thus contained 48.8 ± 0.5% *o*-xylene-d_6, 1.2 ± 0.1% *o*-xylene-d_5, and 50.0 ± 0.5% *o*-xylene-d_0.

were not corrected for the small amount of o-xylene-d_5 present in the o-xylene-d_6.[6]

Isotopic compositions of the toluene and o-ethyltoluene products are given in Table I. The m-xylene product was found to have the same isotopic composition as the o-xylene. The relative product yields are given in Table II. Quantum yields for the vacuum ultraviolet photolysis of o-xylene-d_0 are reported in a previous paper.[2a]

Table I. Isotopic Composition of Toluene and o-Ethyltoluene Products in the Vacuum Ultraviolet Photolysis of Equimolar[a] Mixtures of o-Xylene-d_0 and o-Xylene-d_6

Deuteration	Toluene,[b] %	o-Ethyltoluene,[b] %
d_0	57.2 ± 5.2	43.8 ± 2.1
d_1	7.5 ± 1.7	0.6 ± 0.2
d_2	1.0 ± 0.4	4.4 ± 0.8
d_3	29.7 ± 3.6	21.4 ± 2.5
d_4	4.8 ± 1.4	1.3 ± 0.6
d_5		17.6 ± 0.6
d_6		0.9 ± 0.5
d_7		0.6 ± 0.4
d_8		9.2 ± 0.3

[a] Observed values corrected to correspond to equimolar mixtures. [b] Uncertainty is reported as standard deviation.

Table II. Relative Quantum Yields for Toluene and o-Ethyltoluene Formation in the Vacuum Ultraviolet Photolysis of o-Xylene-d_0 and o-Xylene-d_6

System[a]	Added gas	Pressure of added gas, torr	Toluene[b]	o-Ethyltoluene[b]
o-Xylene-d_0	...	...	0.77	0.41
o-Xylene-d_0 + o-xylene-d_6	...	...	0.65	0.21
o-Xylene-d_6	...	...	0.32	c
o-Xylene-d_0	H_2	50	0.23	0.03
o-Xylene-d_0	H_2	255	0.17	0.02
o-Xylene-d_0	D_2	50	0.17	0.05
o-Xylene-d_0	C_3H_8	50	0.24	c

[a] The pressure of o-xylene-d_0 was measured to be 4.1 torr. The change in vapor pressure with deuteration is assumed to be small. [b] Relative to the quantum yield of m-xylene. The deuteration of methyl groups did not affect the quantum yield of m-xylene to a significant extent (<10%). The quantum yield was decreased considerably by the presence of foreign gases. [c] Not measured.

The photolysis of o-xylene-d_6 (containing 2.5% o-xylene-d_5) was performed and the toluene product analyzed for isotope composition, giving for toluene-d_3, 49.9 ± 3.1%, for toluene-d_4, 49.9 ± 2.7%, and for toluene-d_5, 1.2 ± 0.4%. The yield data for this experiment are given in Table II.

o-Xylene-d_0 was photolyzed in an atmosphere of deuterium gas at a pressure of 139 torr. The pressure of the o-xylene in the system was measured to be 4.1 torr. The isotopic composition of the product toluene was found to be 62.0 ± 0.6% toluene-d_0 and 38.0 ± 0.4% toluene-d_1. The recovered o-xylene showed no exchange of greater than 2%. To determine the nature of the effect of deuterium gas on the product yields (*i.e.*, to determine if the lowering of yields is due just to vibrational quenching), o-xylene-d_0 was photolyzed in the presence of various gases. The results of these experiments are given in Table II.

Discussion

The data in Table I clearly show that loss of methylene from o-xylene is not the predominant process leading to toluene and o-ethyltoluene. Such a mechanism would predict the toluenes to be d_0 and d_4 and the o-ethyltoluenes to be d_0, d_2, d_6, and d_8, and these predictions find no support from the experimental data.

$$C_6H_4CH_3CH_3 \longrightarrow C_6H_5CH_3 + CH_2$$
$$C_6H_4CD_3CD_3 \longrightarrow C_6H_4DCD_3 + CD_2$$
$$CH_2 + C_6H_4CH_3CH_3 \longrightarrow C_6H_4CH_3C_2H_5$$
$$CH_2 + C_6H_4CD_3CD_3 \longrightarrow C_6H_4CD_3C_2H_2D_3$$
$$CD_2 + C_6H_4CH_3CH_3 \longrightarrow C_6H_4CH_3C_2H_3D_2$$
$$CD_2 + C_6H_4CD_3CD_3 \longrightarrow C_6H_4CD_3C_2D_5$$

The toluenes, d_0, d_1, d_3, d_4, and the o-ethyltoluenes, d_0, d_3, d_5, and d_8, that are observed as predominant products can readily arise from radical reactions equivalent to

$$C_6H_4CH_3 + H \longrightarrow C_6H_5CH_3$$
$$C_6H_4CH_3 + D \longrightarrow C_6H_4DCH_3$$
$$C_6H_4CD_3 + H \longrightarrow C_6H_5CD_3$$
$$C_6H_4CD_3 + D \longrightarrow C_6H_4DCD_3$$
$$C_6H_4CH_3CH_2 + CH_3 \longrightarrow C_6H_4CH_3C_2H_5$$
$$C_6H_4CH_3CH_2 + CD_3 \longrightarrow C_6H_4CH_3C_2H_2D_3$$
$$C_6H_4CD_3CD_2 + CH_3 \longrightarrow C_6H_4CD_3C_2D_2H_3$$
$$C_6H_4CD_3CD_2 + CD_3 \longrightarrow C_6H_4CD_3C_2D_5$$

While the number of possible radical reactions that can lead to the observed products is large, the possible primary processes that lead to radical formation are few. The most reasonable processes are the breaking of benzylic carbon-hydrogen bonds to give xylyl (methylbenzyl) radicals and hydrogen atoms,[7] the breaking of phenyl-methyl bonds to give methyl and tolyl radicals, and the breaking of phenyl-hydrogen bonds to give dimethylphenyl radicals and hydrogen atoms. The relative importance of these processes is indicated by the absence or presence of products derived from them. Thus the presence of 2,2′-dimethylbibenzyl[8] (xylyl dimer) is evidence of the importance of xylyl radicals. Assuming that xylyl and tolyl radicals undergo dimerization at the same rate, the failure to observe tolyl dimer or a tolyl-xylyl combination product indicates that tolyl is not present in this system to an important extent. A similar argument is used to conclude the dimethylphenyl radical is not present in the system in appreciable amounts (relative to xylyl).

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(6) A typical mixture contained 1.2 ± 0.1% o-xylene-d_5. Treating the products of this material as though they arose from o-xylene-d_6 introduces a negligible error in our calculations. Our conclusions are certainly in no way affected by its presence in such a small amount.

(7) The direct homolytic cleavage of a benzylic carbon-hydrogen bond is the simplest route to form a benzyl radical and a hydrogen atom, but other reasonable, more complex, routes exist. For example, energy transfer from an electronically excited xylene to a dimethylbenzvalene (which must have at least a fleeting existence) could also lead to cleavage of a carbon-hydrogen bond and directly or indirectly to the same products as the direct cleavage. This more exotic pathway is not required by the data presented in this paper but may be necessary to explain certain results from 2537-Å photolysis.

(8) The principle dimeric product found was o-xylyl dimer. Two other products were detected whose retention times indicate them to be of the same carbon number as the xylyl dimer. The yield of these products was low compared to that of xylyl dimer (10%). The quantum yields of dimeric products were not determined because of analytical difficulties.[2a]

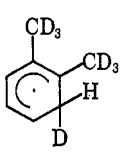
This radical would result from the cleavage of a phenyl–hydrogen bond as a primary process.

On this basis, the principle primary process in the vacuum ultraviolet photolysis of *o*-xylene is the breaking of benzyl–hydrogen bonds to give xylyl radicals and hydrogen atoms.[7] We believe our results can be explained conveniently by invoking only this process as the primary process.

The hydrogen atoms produced in the primary process can react either by combination with radicals or other hydrogen atoms, by group abstraction (H or CH_3), or by addition to the aromatic ring.[9] The rate constant for the addition of hydrogen atoms to *o*-xylene at 25° has been determined to be 10^{12} cc mol^{-1} sec^{-1}.[10a]

Hydrogen atom dimerization cannot be important in this system because at the pressure involved (<100 torr) this reaction is third order. Because of the complexity (and consequently the large number of available vibrational modes) of xylyl radical, hydrogen–xylyl radical combination might be second order and thus more probable at this pressure. Assuming[11] the second-order constant for this combination reaction to be 1×10^{12} cc mol^{-1} sec^{-1}, the concentration of radicals necessary for this reaction to be significant can be approximated. The rate of formation of hydrogen atom–xylyl radical combination product is 10^{12} (H) (radical), while the rate of addition of hydrogen atoms to xylene is 10^{12} (H) (*o*-xylene). For the combination reaction to account for 10% of the reaction of hydrogen atoms, the relative radical concentration (radical)/(*o*-xylene) would have to be 0.1. This would indeed be an unusually high radical concentration.

The results of the photolysis of *o*-xylene-d_6 can be used to predict the consequences of the addition of hydrogen atoms to *o*-xylene. The isotope composition of the product toluene, 49.9 ± 0.5% d_3, 49.9 ± 0.5% d_4, requires a source of hydrogen atoms. The breaking of benzylic carbon–hydrogen bonds results only in the production of deuterium atoms. When these atoms add to the aromatic ring of an *o*-xylene-d_6 molecule, two types of intermediates can be formed.



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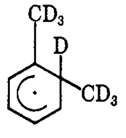

II

Intermediate I can lose either deuterium or hydrogen. The hydrogen atoms produced then themselves may add to an *o*-xylene-d_6 molecule. The products of that reaction are the H analog of II which ejects CD_3 to form toluene-d_3 or the H analog of I which exchanges a ring hydrogen for the attacking hydrogen, *i.e.*, no reaction. Thus every time a deuterium adds to an *o*-xylene-d_6 molecule to form intermediate I, the only toluene produced is toluene-d_3. Intermediate II can only expel CD_3 to form toluene-d_4. The ratio of toluene-d_3 to toluene-d_4 produced in this experiment indicates that deuterium atoms react with *o*-xylene-d_6 to exchange as often as they substitute for methyl to yield toluene. In addition, an amount of *o*-xylene-d_7, equal to the amount of toluene-d_3, must be produced. As the total yield of toluene is about 1%, the amount of *o*-xylene-d_7 produced should be about 0.5%. Our techniques, which have an uncertainty of about 2%, would not detect this.

The isotope composition data for the *o*-xylene-d_0 + *o*-xylene-d_6 mixture photolysis allows the calculation of the relative rate of loss of deuterium from *o*-xylene-d_6 as compared to the loss of hydrogen from *o*-xylene-d_0. The *o*-ethyltoluene that results in the photolysis can arise only from the combination of methyl and xylyl radicals.[12] *o*-Ethyltoluenes-d_0 and -d_3 result from the combination of CH_3 and CD_3 (produced in the processes yielding toluene) with the xylyl radical resulting from the primary process for *o*-xylene-d_0. *o*-Ethyltoluenes-d_5 and -d_8 result from the combination of CH_3 and CD_3 with the xylyl radical from *o*-xylene-d_6. The ratio of the product yields of *o*-ethyltoluenes-d_0 + -d_3 to those of *o*-ethyltoluenes-d_5 + -d_8 must equal the ratio of the rates of production of these radicals (*i.e.*, the ratio of the rates of primary process for *o*-xylene-d_0 to *o*-xylene-d_6).

$$\frac{V_{\text{prim proc-}d_0}}{V_{\text{prim proc-}d_6}} = \frac{d_0 + d_3}{d_5 + d_8} = 2.5 \pm 0.1$$

This number is a combination of primary and secondary isotope effects.

The *o*-ethyltoluene data in this experiment can also be used to determine the relative availabilities of CH_3 and CD_3. The ratio of the yields of the products resulting from CH_3 (*o*-ethyltoluenes-d_0 and -d_5) to the yields of products resulting from CD_3 (*o*-ethyltoluenes-d_3 and -d_8) is equivalent to the relative concentrations of these species.

$$\frac{(CH_3)}{(CD_3)} = \frac{d_0 + d_5}{d_3 + d_8} = 2.0 \pm 0.2$$

This number can be calculated independently from isotope distribution data for the product toluene in this experiment (Table I). The proposed mechanistic scheme requires that for each methyl radical, a corresponding toluene molecule is produced. Thus for each toluene-d_0 and toluene-d_1, there is a CH_3 radical, while for each toluene-d_3 and toluene-d_4, there is a CD_3 radical. The ratio of rates of formation of CH_3 to CD_3 (equal to relative concentrations of these species) is simply the ratio of the product yields of the requisite toluenes. The good agreement between this number

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(9) The reaction of hydrogen atoms with *o*-xylene to give methane by group abstraction is usually considered to be unimportant.[10] The abstraction of hydrogen by hydrogen atoms may account for the observed production of hydrogen molecules.

(10) (a) S. W. Benson and R. Shaw, *J. Chem. Phys.*, **47**, 4052 (1967); (b) M. C. Sauer, Jr., and B. Ward, *J. Phys. Chem.*, **71**, 3971 (1967).

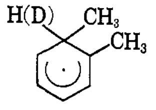
(11) The second-order rate constant for the combination of methyl radicals with benzyl radicals is reported as $k = 1.2 \times 10^{11}$ cc mol^{-1} sec^{-1} at 300°K: see R. J. Kominar, M. G. Jacko, and S. J. Price, *Can. J. Chem.*, **45**, 575 (1967). This value is lower than the theoretical value of 5×10^{13} cc mol^{-1} sec^{-1} for radical combination reactions. This deviation from ideality occurs almost entirely in the frequency factor, due to the size and complexity of benzyl radical. This steric effect will show up, although probably to a smaller extent, in the combination of hydrogen atoms with xylyl radical. We use the value 1×10^{12} cc mol^{-1} sec^{-1} as a compromise value, larger than the value for methyl + benzyl and smaller than the theoretical value for radical combination reactions. The precise value of this number is not important to our arguments.

(12) The reaction $CH_3 + C_6H_4CH_3CH_3 \rightarrow C_6H_4CH_3C_2H_5 + H$ is not considered because methyl radicals are known to abstract preferentially hydrogen atoms when they react with alkylbenzenes: A. C. Eachus, Ph.D. Thesis, State University College of Forestry, Syracuse University, Syracuse, N. Y., 1964.

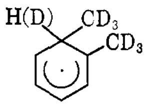
$$\frac{(\mathrm{CH_3})}{(\mathrm{CD_3})} = \frac{d_0 + d_1}{d_3 + d_4} = 1.9 \pm 0.3$$

and the value calculated from the *o*-ethyltoluene data indicates that there are no important processes that methyl radicals undergo, in this system, which involve significant isotope effects.

There are several possible explanations for the difference in loss of CH_3 from *o*-xylene-d_0 compared with loss of CD_3 from *o*-xylene-d_6. One is a kinetic isotope effect in the loss of methyl from the intermediate in the reaction producing toluene. However, this would require the loss of methyl from III and IV to be the rate-determining step in the formation of toluene. For this to be the rate-determining step, the activation barrier to the loss of methyl would have to be greater than the barrier to the loss of hydrogen (deuterium) from III and IV. In view of known thermochemistry of bond dissociation[13] this is not reasonable.[14]



III



IV

A second possible explanation is that a deuterium substituent effect is operative in this system. CD_3 substituents might decrease the rate of addition of hydrogen or deuterium to the aromatic ring of *o*-xylene-d_6 relative to the rate hydrogen or deuterium adds to the aromatic ring of *o*-xylene-d_0. This explanation is probably not adequate because the deuterium electronic substituent effects in systems of this type are known to be small. Sauer and Ward determined that substituting the α-hydrogens with deuteriums in toluene did not change the rate of addition of hydrogen atoms (to within an experimental error of 15%).[10b] Another possibility is that the rate of addition of hydrogen (deuterium) to *o*-xylene-d_0 to form intermediate III is 1.9 times as great as the rate of addition of hydrogen (deuterium) to *o*-xylene-d_6 to form intermediate IV. It is known that some strain energy, resulting from the steric compression of the methyl groups, exists in *o*-xylene.[15] There is probably more strain in *o*-xylene-d_0 than there is in *o*-xylene-d_6 due to the difference in size between CH_3 and CD_3. The formation of intermediate III which relieves this strain should be energetically more favorable than the formation of intermediate IV. An energy difference of 0.3–0.5 kcal/mol is needed to account for the observed rate difference of 1.9 ± 0.3. Since the total strain energy in *o*-xylene-d_0 is about 0.7 kcal/mol,[15] this effect probably can not explain the entire observed isotope effect, but is in the right direction and can contribute to it. Perhaps a combination of these three effects, all operating in the same direction, is sufficient to give the observed effect.

The ratio of toluene products in the *o*-xylene-d_0 + -d_6 mixture photolysis derived from the substitution of CH_3 or CD_3 by hydrogen (toluenes-d_0 and -d_3) to those derived from the displacement of CH_3 or CD_3 by deuterium (toluenes-d_1 and -d_4) can be predicted. We had obtained the result, by analyzing the isotope composition data for the *o*-ethyltoluene produced in this experiment, that ten hydrogen atoms are produced for every four deuterium atoms (2.5/1). The fate of these atoms is shown in the following reaction scheme.

$$10\mathrm{H} \longrightarrow 10(\text{toluenes-}d_0 + \text{-}d_3)$$

$$\begin{tikzcd} & 0.8(\text{toluene-}d_4) + 0.8(\text{toluenes-}d_0 \text{ or } \text{-}d_3) \\ 4\mathrm{D} \arrow[ur, "o\text{-xylene-}d_6"] \arrow[dr, "o\text{-xylene-}d_0"'] & \\ & 1.6(\text{toluene-}d_1) + 0.8(\text{toluenes-}d_0 \text{ or } \text{-}d_3) \end{tikzcd}$$

This scheme predicts the ratio of products to be 11.6/2.4 = 5/1. The experimental value, as calculated from the data in Table I, is in reasonable agreement.

$$\frac{d_0 + d_3}{d_1 + d_4} = 7.0 \pm 1.3$$

Using the results of the photolysis of *o*-xylene-d_0 in the presence of deuterium gas, the kinetic temperature of the hydrogen atoms that react to produce toluene can be determined. The isotope composition of the product toluene (62% toluene-d_0 and 38% toluene-d_1) indicates that two competing reactions are operative for the hydrogen atoms produced in the primary process. One is the reaction of hydrogen with D_2.

$$\mathrm{H} + \mathrm{D_2} \longrightarrow \mathrm{HD} + \mathrm{D} \qquad (1)$$

These deuterium atoms result in the toluene-d_1 that is observed. The other reaction is the addition of hydrogen atoms to the aromatic ring of *o*-xylene to produce toluene-d_0 (reaction 2). The rate constant for reaction

$$\mathrm{H} + \mathrm{C_6H_4CH_3CH_3} \longrightarrow \mathrm{C_6H_5CH_3} + \mathrm{CH_3} \qquad (2)$$

1 is $k_1 = 10^{8.32-7.5/\theta}$ cc mol^{-1} sec^{-1} ($\theta = 2.3RT$ kcal mol^{-1}).[16] Benson and Shaw[10a] have recently determined the rate constant for reaction 2 to be $k_2 = 10^{12.6-0.6/\theta}$ cc mol^{-1} sec^{-1}. The rate of formation of toluene-d_0 is

$$V_{d_0} = fk_2(\mathrm{H})(o\text{-xylene})$$

The factor f represents the probability of a hydrogen atom adding to the ring at a methyl position. The rate of formation of toluene-d_1 is

$$V_{d_1} = fk_1(\mathrm{H})(\mathrm{D_2})$$

Again, f is the probability a deuterium will add to a methyl position of an *o*-xylene molecule. The probability factors in the two cases are assumed to be the same. The ratio of the rate constants for these two reactions is

$$k_2/k_1 = (V_{d_0}/V_{d_1})(\mathrm{D_2})/(o\text{-xylene})$$

The ratio of the rates can be replaced by the ratio of the yields of these two products. The ratio of the concentrations is very closely equal to the ratio of the partial pressures of these two species in the system. The expression reduces to

$$\begin{aligned} k_2/k_1 &= (\text{toluene-}d_0/\text{toluene-}d_1)(P_{\mathrm{D_2}}/P_{o\text{-xylene}}) \\ &= (62/38)\,(139/4.1) \\ &= 57.6 \\ \log k_2 - \log k_1 &= 1.75 \end{aligned}$$

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[13] K. B. Wiberg, "Physical Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1964, p 242.

[14] S. W. Benson and R. Shaw, *J. Amer. Chem. Soc.*, **89**, 5351 (1967). The conclusion is drawn that in the analogous case for toluene, the formation of a similar intermediate is essentially irreversible.

[15] W. J. Taylor, *et al.*, *J. Res. Nat. Bur. Stand.*, **37**, 95 (1946).

[16] J. C. Polanyi, *J. Chem. Phys.*, **23**, 1505 (1955).

Substituting the Arrhenius expressions for the rate constants, we obtain

$$12.6 - (0.6/\theta) - 13.3 + (7.5/\theta) = 1.75$$

$$\theta = 2.8$$

$$2.3RT = 2.8\ (R \text{ in kcal mol}^{-1}\text{ deg}^{-1})$$

$$T = 600\text{°K}$$

The conclusion is that the hydrogen atoms react as "hot" atoms. This is not surprising as the hydrogen atoms produced in the primary process carry a very large amount of excess energy.[17] The hydrogen atoms produced in the primary process in the vacuum ultraviolet photolysis could contain as much as 80 kcal/mol excess energy if all the energy supplied is used in the bond breaking process. Only a very small fraction of this energy is needed to explain the observed values. These atoms appear to react before they are completely thermalized.

Based on the preceding arguments, the suggested mechanistic scheme for the vacuum ultraviolet photolysis of *o*-xylene is[18]

$$C_6H_4CH_3CH_3 \longrightarrow C_6H_4CH_3CH_3{}^*$$

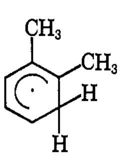
$$C_6H_4CH_3CH_3{}^* \longrightarrow C_6H_4CH_3CH_2 + H$$

$$H + C_6H_4CH_3CH_3 \longrightarrow C_6H_5CH_3 + CH_3$$

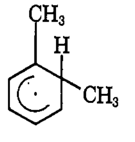
$$CH_3 + C_6H_4CH_3CH_2 \longrightarrow C_6H_4CH_3C_2H_5$$

$$2(C_6H_4CH_3CH_2) \longrightarrow C_6H_4CH_3CH_2CH_2CH_3C_6H_4$$

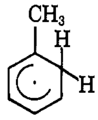
We believe the mechanistic scheme presented also can explain satisfactorily the results of the pyrolysis of *o*-xylene using the hydrogen carrier technique.[19] The authors of these papers conclude that there is no reaction of hydrogen atoms with the ring of *o*-xylene, because they did not observe the extensive isotopic exchange observed in the toluene–hydrogen pyrolysis. Actually, one would not expect extensive exchange in the *o*-xylene system but would expect it in the toluene system. In *o*-xylene, the energy difference between the two intermediates expected from hydrogen addition is probably small.[20] Intermediate VI should be slightly favored because of the relief of steric strain. We did observe, in the photolysis of *o*-xylene-d_6, that the addition of deuterium to the ring at a methyl-substituted position occurred at a rate equal to that of exchange of deuterium for hydrogen at a ring position.[21] In the case of toluene, we would expect the intermediates VII and VIII to be energetically quite different. Intermediate VII contains a methyl-substituted radical while intermediate VIII does not. Also, as there is no strain energy in toluene, there is nothing to be gained by adding to the methyl-substituted position. The difference in stability between the methyl-substituted radical and the nonmethyl-substituted radical[22] corresponds to a rate increase of about 3.3. The statistical factor of 5 makes reaction at a hydrogen-substituted position more favorable than methyl substitution by a factor of about 16. Assuming a small isotope effect[14] in loss of H or D from VII, exchange should occur about eight times as often as methyl substitution. Burr and Strong's results for the pyrolysis of toluene[23] indicate this to be approximately correct.



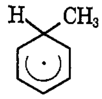
V



VI



VII



VIII

While it is not prudent to assign definitively any particular electronic or vibrationally excited state as the source of the reactions described here, the mechanism which has been presented offers some evidence which bears on the problem. An earlier, tentative suggestion[2a] that both vacuum ultraviolet and near-ultraviolet photolyses of *o*-xylene may proceed through common vibrationally excited intermediates was based on a similarity of products.[24] Since the energies available from the two sources differ significantly (160 *vs.* 110 kcal/mol), such a confluence is not logically demanded. The *o*-xylene molecule which has just been excited by 1800-Å radiation certainly has sufficient energy to break a phenyl–methyl or a phenyl–hydrogen bond. It is significant that these processes do *not* occur, but instead the weakest bond in the molecule is cleaved in the principal photoprocess. Since the 2537-Å radiation also has adequate energy for the benzylic hydrogen cleavage, the postulate of common reaction paths in the two systems remains attractive.

Experimental Section

Materials. Phillips 66 Research Grade *o*-xylene-d_0 was used without further purification. Its purity was determined by gas chromatography to be >99.98 mol %. Volk Radiochemical *o*-xylene-d_6 (methyl deuterated) was also used without further purification. Its purity as determined by gas chromatography was 99.97 mol %. The isotopic composition of this material was measured by mass spectroscopy to be 97.5 ± 0.5% *o*-xylene-d_6 and 2.5 ± 0.2% *o*-xylene-d_5. Research grade Matheson deuterium and hydrogen were used directly from lecture bottles. Phillips Petroleum propane was used directly from a lecture bottle.

Analysis. Product analysis was performed using flame-ionization gas chromatography. The most useful column was a 5%

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[17] J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," John Wiley and Sons, Inc., New York, N. Y., 1966, p 647.

[18] This scheme only attempts to give a path for formation of the products discussed in this paper. The isomeric xylenes and benzocyclobutene are formed by different paths.[2a] The ethylbenzene that is observed[2] may result from the secondary photolysis of toluene. Hydrogen and methane that are observed may be produced in the reactions that produce the polymeric product,[2b] and/or by group abstraction by hydrogen atoms.[9]

[19] J. G. Burr and J. D. Strong, *J. Amer. Chem. Soc.*, **86**, 5065 (1964); *J. Chem. Phys.*, **43**, 1432 (1965).

[20] The increase in energy gained by substituting a hydrogen atom in the 2 position of a pentadienyl radical by a methyl is negligible.

[21] We observed an equal amount of exchange and methyl substitution. Combining this with the statistical factor involved, we conclude that a probable isotope effect in exchange is offset by a slight preference for reaction at a methyl site rather than a hydrogen site.

[22] J. L. Bolland, *Trans. Faraday Soc.*, **46**, 358 (1950).

[23] J. G. Burr, R. A. Meyer, and J. D. Strong, *J. Amer. Chem. Soc.*, **86**, 3846 (1964).

[24] There are additional reactions which occur in the vacuum ultraviolet photolysis. Both benzocyclobutene[2a] and *p*-xylene are *primary* products of the vapor-phase photolysis (H. R. Ward and C. I. Barta, unpublished results).

diethylene glycol adipate–pentaerythritol adipate–5% Bentone-34 on 100–120 mesh Chromosorb W, $^1/_8$ in. o.d. × 20 ft, operated at 70°. Product analysis on this column has previously been reported.[2a] Analysis for dimeric products was achieved using a 5 ft × $^1/_8$ in. o.d. SE-30 column operated at 137°. Identification was achieved by comparison of retention times with those of authentic samples. Areas were determined by disk integration and corrected for detector sensitivity to give the mole fraction.

Isotopic composition of the products was determined by mass spectroscopy using a Hitachi–Perkin-Elmer RMU-6D. A gas chromatograph–mass spectrometer combination proved to be unsuitable because of the differences in retention times between components of different degrees of deuteration. The isotope composition at any point on chromatogram peak varied with time. It was found that the more heavily deuterated species in the peak had shorter retention times. A mass spectrum taken at a point on the leading edge of a chromatogram peak indicated a higher percentage of deuterated components than the true value. Physical collection of the products by preparative gas chromatography was necessary (but difficult as conversion was kept to about 1% to prevent secondary photolysis of the products). Samples were obtained by preparative gas chromatography using an Aerograph Model 204 equipped with a flame-ionization detector, modified with a sample stream splitter. This splitter, inserted between the column exit and the detector, diverted more than 90% of the sample stream to a liquid nitrogen cooled U trap. These traps, after evacuating at liquid nitrogen temperature to $<10^{-3}$ torr, were placed directly on the gas sampling system of the mass spectrometer. Spectra were obtained at just above the appearance potential of the samples to minimize fragmentation.

A control experiment was performed to determine the extent of fractionation of products of varying degree of deuteration in the collection technique. When a mixture containing 49.7 ± 0.5% *o*-xylene-d_0, 1.2 ± 0.1% *o*-xylene-d_5, and 48.8 ± 0.5% *o*-xylene-d_6 was passed through the chromatography column and collected, its composition had changed to 49.2 ± 0.5% *o*-xylene-d_0, 1.3 ± 0.1% *o*-xylene-d_5, and 49.4 ± 0.5% *o*-xylene-d_6. An error of less than 2% is introduced by this collection technique.

Observing isotope exchange in the recovered *o*-xylene was not possible because of the low conversion. Exchange of less than 2% is below the limit of our analytical techniques. Thus, at best, we can say that exchange of greater than 2% did not occur.

Photolysis of Equimolar Mixtures of *o*-Xylene-d_0 and *o*-Xylene-d_6. Two capillary tubes, one containing 9 mg of *o*-xylene-d_0 and the other containing 9 mg of *o*-xylene-d_6, were placed in a vessel on a mercury-free vacuum line. The vessel was evacuated to $<10^{-3}$ torr and closed off from the vacuum line by a stopcock. The capillary tubes were broken by twisting a notched rod in the vessel, which was then cooled to liquid nitrogen temperature. The vessel was reevacuated to remove any air present in the capillary tubes. The sample, now in the vessel, was allowed to warm and was vacuum transferred to a photolysis cell. The cell was an integral part of an oxygen discharge lamp whose output was mostly in the 1600–2000-Å region.[2a] The samples were photolyzed for 10.0 min and the photolysate was condensed at liquid nitrogen temperature into a small flask attached to the reactor vessel. This flask was removed from the reactor vessel and the analysis was performed immediately.

Photolyses of pure *o*-xylene-d_0 and of *o*-xylene-d_6 were performed using the same procedure. The sample size in these cases was 18 mg of pure material. At least three photolyses were performed on each system.

Photolysis of *o*-Xylene in the Presence of Deuterium Gas. Approximately 100 mg of *o*-xylene-d_0 was placed in a small flask, cooled to liquid nitrogen temperature, and thoroughly degassed by a freeze–thaw cycle. The material was allowed to warm to room temperature and to expand into the vacuum line and reactor cell. The pressure in the system was then measured using a Wallace–Tiernan Bourdon gauge. The reactor cell was closed off from the vacuum line and the sample condensed at liquid nitrogen temperature. The material remaining in the vacuum line was removed by pumping, and the cell was opened to the vacuum line. The vacuum line was closed off from the vacuum pump and the entire system filled with deuterium gas from a cylinder that had previously been attached to the vacuum line. The pressure in the system was measured by the pressure gauge.[25] The reactor cell, now containing *o*-xylene at its vapor pressure, and a measured amount of deuterium gas, was closed off by a stopcock from the vacuum line and photolyzed as before for 10.0 min.

The Photolysis of *o*-Xylene-d_0 in the Presence of Hydrogen and Propane. *o*-Xylene-d_0 was photolyzed in the presence of hydrogen and propane using a procedure similar to that described for deuterium. The major difference in procedure was the use of an Ashcroft Bourdon gauge instead of the Wallace–Tiernan gauge.

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(25) The error introduced by cooling the small segment of the system that contained the *o*-xylene sample is estimated to be less than 5%.