and C_0/C_0'. For any initial value C_0/C_0' one determines experimentally $\bar{C}/C_0$ as a function of τ and then finds out the respective values of the parameter g from Table VII. Plotting $g/(C_0' - C_0)$ versus τ one obtains a straight line slope of which is $(^1/_2)k_3$.

In conclusion, it should be stressed that for the same residence time τ the fraction of conversion $\bar{C}/C_0$ is always larger for a plug flow than for a laminary flow if all the other parameters remain constant.

Organic Compounds in Microwave Discharge. II. Initial Studies with Toluene and Related Hydrocarbons[1]

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A microwave discharge of a dilute mixture of toluene in helium has been found to form principally benzene, ethylbenzene, styrene and phenylacetylene. The minor amounts of the xylenes and biaryls in the product indicate that free radicals are not important reaction intermediates. The reaction of specifically deuterated toluenes has shown that the benzene and ethylbenzene do not result from a tropylium cation intermediate. Relative reactivities and the constancy of product ratios can most reasonably result from the formation of a molecule-anion. The reactions of benzene, ethylbenzene, cycloheptatriene and bicycloheptadiene are also described. Compounds with several multiple bonds are more reactive than saturated analogs.

Introduction

The utilization of electric discharges in chemical investigations is not recent; in their review of discharge reactions, Glocker and Lind[4] quote references extending back into the eighteenth century. These first investigations were sufficient to show the complexities of reactions of organic molecules in discharge, and perhaps as a result the bulk of study has been done with inorganic gases. Such discharge reactions have proved to be especially useful in the formation of free radicals from diatomic gases.[5]

The introduction of organic compounds to a discharge often results in the formation of a large number of products accompanied by varying amounts of tars.[6] Until recently, instrumental methods have been insufficient to resolve these mixtures. Schüler and coworkers have performed intensive studies on organic compounds in a high-frequency electrode discharge, most often with the view of investigating the spectra of the excited species so produced.[7]

Of the types of discharge available, that formed in a microwave cavity has several advantages. The discharge is formed by the high frequency field set up between the walls of cavity, and occurs in a quartz or Pyrex tube. The high frequency discharge is more efficient than one formed by direct current, since it avoids the loss of electrons by migration to an anode. It is possible to maintain a discharge at pressures of from 1 to 80 mm. so that reasonably large concentration changes are available. Most important, because the discharge is formed without electrodes, the problems common to electrode discharges are avoided. Microwave discharges have been found useful in inorganic synthesis.[8] In the particular case of hydrogen, 80% of the molecules can be converted into hydrogen atoms.[9]

Similar methods have been used in the production of nitrogen,[10] oxygen,[10] halogen[11] and hydroxyl radicals.[12] If an organic compound is placed close to (but not in) such a discharge in tritium, the rate of tritium incorporation into the molecule is greatly enhanced.[13]

The actual physics of the microwave discharge has received intensive study,[14] and the fact that atoms are produced in the effluent of a stream of molecular gas flowing through the discharge is well established, but few studies have been concerned with processes occurring directly in the discharge zone. Since electron energies can range up to about 20 e.v. in these discharges, they would seem to provide a method of study of radiation chemistry between the energies of photochemistry (up to about 6 e.v.) and radiolysis reactions (kev. to mev. range). Although intermediate energies can be obtained in a mass spectrometer, the discharge allows the investigation of neutral products and the production of materials in preparative quantities. Nevertheless, the only literature report of an organic compound reacting directly inside a microwave discharge is the conversion of methane into acetylene.[15] Even in this case, however, the high power level at which the discharge was maintained suggests that the reaction may have occurred in an arc rather than a glow discharge. In this paper we report some of our observations on reactions of organic compounds within a microwave glow discharge; of particular significance is our observation that certain of these reactions apparently differ from those reported in other high-energy chemistry.

Experimental

A schematic representation of the apparatus used in the discharge reactions is shown in Fig. 1. Carrier gases (helium, USN; methane, Matheson, 99%; hydrogen, purified; all used without further purification) were fed through flow meters and needle valves, and made to flow over the organic sample. The rate of sample introduction was controlled by thermostating the sample well. Helium flow was about 0.7 l./min. at 25° and one atmosphere. Methane and hydrogen flows were 80 ml./min. under the same conditions. Toluene was thermostated at 0° for most

(1) This work has been supported in part by the National Science Foundation. A preliminary communication is treated as paper I: A. Streitwieser, Jr., and H. R. Ward, J. Am. Chem. Soc., **84**, 1065 (1962).

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(7) H. Schüler and M. Stockburger, Spectrochim. Acta, **15**, 981 (1959); H. Schüler and E. Lutz, Z. Naturforsch., **12a**, 334 (1957); H. Schüler and L. Reinebeck, Spectrochim. Acta, **6**, 288 (1954); H. Schüler and V. Degenhart, Z. Naturforsch., **7a**, 753 (1952).

(8) W. L. Jolly, "Synthetic Inorganic Chemistry," Prentice–Hall, Inc., Englewood Cliffs, N. J., 1960, p. 113.

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(11) E. A. Ogryzlo, ibid., **39**, 2556 (1961).

(12) H. E. Radford, Phys. Revs., **122**, 114 (1961).

(13) F. Cacace, "Proceedings of the Symposium n Chemical Effects of Nuclear Transformation," Prague, 1960, p. 133; T. W stermark, H. Lindroth and B. Enander, J. Appl. Rad. and Isotopes, **7**, 331 (1960); N. A. Ghanem and T. Westermark, J. Am. Chem. Soc., **82**, 4432 (1960).

(14) S. C. Brown, "Basic Data of Plasma Physics," Technology Press, Cambridge, Mass., 1959, p. 302.

(15) P. L. McCarthy, J. Chem. Phys., **22**, 1360 (1954); Dr. A. P. Wolf has been studying the rearrangement of C^{14}-labeled toluene within a microwave glow discharge as part of an extensive study of radiolysis-induced reactions (personal communication).
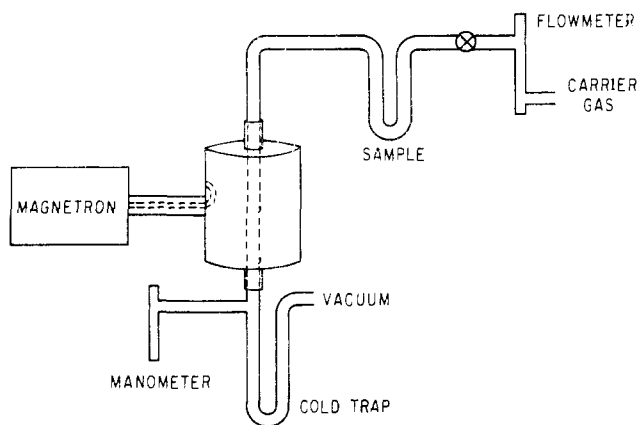
Fig. 1.—Schematic diagram of discharge apparatus.

experiments, which controlled the rate of sample flow at 0.8 mM./min.

The dilute solution of organic substrate in the carrier gas was passed into a 20 mm. i.d. quartz tube contained in a 77 mm. × 77 mm. cylindrical copper cavity. Microwaves were fed to the cavity by a Raytheon QK-61 magnetron (3 kmc., 100 watts). The cavity was cooled by an air blast which kept the internal temperature at about 185°. The discharge tube pressure was measured with a manometer placed just outside the discharge zone. The condensable material was trapped in a U-tube filled with glass wool and cooled with liquid nitrogen. The pressure in the cavity was held at about 20 mm. by regulating a valve leading to a vacuum system. Under these conditions, the residence time in the cavity was 0.03 sec. and the toluene concentration was typically about 3% in the carrier gas stream.

Volatile products were removed from the trap by vacuum transfer and the amount of tar formation was determined by the change of weight in the trap and the discharge tube. The transferable liquid was analyzed by gas chromatography. The most useful columns were Silicone QF-1, Tween, SE-30 (all from Wilkens Instrument and Research, Inc.) and Silicone No. 710, Dow Corning. Identification was by comparison of retention times and infrared spectra. Deuterium analyses were by infrared and mass spectral measurements and comparisons with standards. Total material balance ranged from 92–99%, the remainder being comprised of non-condensable gases. The percentage recovery refers to the volatile fraction containing recovered starting material and condensable products.

Results and Discussion

After a preliminary survey of a number of compounds, toluene was chosen as an attractive system for more detailed study. The expected products are volatile and are amenable to gas chromatographic separation and infrared identification. The considerable body of information concerning the reactions of toluene in mass spectrometers and labeling by tritium under a variety of high energy conditions[16] were available for comparison. The results of replicate experiments in which toluene was exposed to the glow discharge are reported in Table I.

TABLE I

GLOW DISCHARGE OF TOLUENE IN HELIUM[a]

| Recovery,[b] %	68	77	77
Low mol. wt.[c,d]	15	15	9
Benzene[d]	48	48	49
Ethylbenzene[d]	28	28	30
Styrene[d]	3	2	3
Phenylacetylene[d]	7	7	8
Toluene[e]	86	93	84

[a] Percentages of products are determined directly from peak areas of gas chromatographs but do not differ significantly from weight percentages. [b] The percentage by weight of the starting material which was recovered in the volatile fraction. [c] The low molecular weight fraction is made up of compounds of from four to six carbons, and contained at least six compounds. [d] Percentage of the volatile fraction, normalized to exclude toluene. [e] Percentage of the volatile fraction.

(16) H. J. Ache, W. Herr and A. Thiemann, Proceedings of the Symposium on Chemical Effects of Nuclear Transformations, Prague, 1960, p. 111.

The toluene that reacts forms principally benzene and the C_8-hydrocarbons, ethylbenzene, styrene and phenylacetylene, together with comparatively small amounts of lower molecular weight compounds. The material not accounted for as product was present as tar and carbonaceous material or as low molecular weight non-condensable materials. Analysis of the effluent gas stream by gas chromatography showed the presence of hydrogen, methane, ethylene and acetylene. Since these products appear to result from complex processes, they are not investigated further.

Because of instrumental difficulties, principally in controlling cavity efficiency, it was not possible to reproduce exactly the conversion of toluene in duplicate experiments. Thus, the percentage of recovered toluene varied from 84 to 93%, while all of the controllable conditions remained the same. The amount of material which could be isolated by vacuum transfer techniques at the end of a run (% recovery) was also difficult to reproduce. Despite these disparaties in conversion, the product composition remained strikingly constant.

The fact that the total percentage of C_8-compounds remains approximately constant is an especially intriguing one, since these products must result from bimolecular reactions. It is perhaps indicative that benzene is formed by the same bimolecular process that leads to the C_8-products and suggests the stoichiometry

$$2C_6H_5CH_3 \longrightarrow C_6H_6 + C_6H_5C_2H_5$$
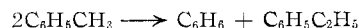
Styrene and phenylacetylene are reasonable further products from excited ethylbenzene.

The novelty of this reaction prompts a further study of its mechanism—we are interested in the mode of energy transfer and in the reaction intermediates involved. In a system as complex as a discharge, surely many forms of energy transfer are operative and many types of intermediates and reactions occur, but we are interested primarily in those processes that are responsible for the bulk of the observed principal products. In many radiolysis and discharge reactions, for example, the main path to products is considered to be a series of radical reactions. In the present case, ethylbenzene can be visualized to arise by a radical route—the combination of benzyl and methyl radicals—however, this process would require the existence of methyl radicals in the presence of a large excess of toluene molecules, and, under these conditions, the formation of substantial amounts of xylene would be expected. Xylenes are actually formed in only minute amounts. Furthermore, if radicals were important reaction intermediates, substantial amounts of dimer biaryls are expected in the product. The traces of such compounds actually formed in this reaction necessitated special experiments to determine the extent of their formation. From 0.88 g. of toluene under conditions which resulted in 88–90% reaction, there was formed 3.7 mg. of bibenzyl, 1.2 mg. of diphenylmethane and 0.7 mg. of biphenyl, along with traces of dihydroanthracene and dihydrophenanthrene. This result differs from that of Schüler, who, with toluene in electrode discharges, has obtained spectra which he attributes to benzyl radicals.[17]

Changing the toluene concentration in the helium carrier stream was found to cause important changes in the percentage of recovery and the extent of conversion of the toluene, while the effect on the product composition was minor (Table II).

It is likely that the concentration of toluene to a large extent controls the energy of the electrons in the

(17) H. Schüler and A. Michel, Z. Naturforsch., 10a, 495 (1955).

TABLE II[a]

EFFECT OF TOLUENE PRESSURE ON PRODUCT COMPOSITION

Rel. concn. of toluene	1	4	48
Recovery, %	6	52	73
Benzene	51	51	49
Ethylbenzene	16	27	34
Styrene–phenylacetylene	31	19	15
Toluene	65	72	81

[a] The percentages reported here have the same significance as those reported in Table I, except that the percentage of products has been normalized in a manner which excludes low molecular weight products.

discharge. The toluene molecules have a much larger cross-section for electron collision, and probably serve to "attenuate" the electron energy. To investigate this possibility further, a large excess of methane was added to the carrier gas stream. The effect of this change on product composition was minor, and no new products were formed, but a pronounced change occurred in the extent of tar and carbon formation. In the case of toluene, tar formation was reduced to less than 1%. A methane–helium stream alone was shown to give only a trace of liquid products, and gave no evidence of tar or carbon formation. A similar reduction in tar formation resulted from the use of hydrogen–helium mixtures as carrier gas. These experiments not only provide evidence against the important involvement of simple radicals in the primary reaction but also rule out reaction with helium in metastable excited states as an important source of energy transfer. With regard to the latter possibility, argon as carrier gas gave essentially the same results with toluene as did helium. These results demonstrate also that these reactions are not simple pyrolysis reactions, a conclusion that is bolstered by the comparatively low reaction temperature ($\leqslant 185°$).

Another possible path of reaction for the toluene molecule is formation of the molecule-cation by electron impact. Several investigations have been made of this reaction in the mass spectrometer. Rylander, Meyerson and Grubb[18] concluded from experiments with labeled toluenes that the tropylium cation is formed before cracking occurs. This explanation is invoked to explain the scrambling of deuterium labels in the fragmentation products. In the glow discharge a similar rearrangement would demand randomization of labels in the benzene and ethylbenzene produced from specifically labeled toluenes. Preliminary results of reactions with deuterated and tritiated toluenes indicate that such randomization is not important.[19] The particular example of α- and p-deuteriotoluene reported in Table III shows a rather high degree of selectivity. In particular, deuterium that starts in the methyl group of toluene remains largely in the ethyl group of ethylbenzene. Similarly, only a small amount of deuterium that starts in the ring ends up in the alkyl group.

TABLE III

DEUTERIUM DISTRIBUTION IN PRODUCTS OF DEUTERIOTOLUENE DISCHARGE

Starting toluene	Benzene, % d_1	Ethylbenzene, %	
		Alkyl-d_1	Ring-d_1
α-d	34	147	10
p-d	92	34	82

In order to maintain a glow discharge, it is necessary that sufficient ionization occur to replace electrons lost to the walls. Since toluene has both a lower ionization

(18) P. N. Rylander, S. Meyerson and H. M. Grubb, J. Am. Chem. Soc., 79, 842 (1957).

(19) A more complete study of reactions of labeled toluenes will be reported later.

potential and a higher collision cross-section for ionization than helium, it is almost certain that some of the molecule cation must form. The specificity in the reactions of the labeled toluenes demands either that the molecule-cation formed under these conditions does not rearrange, or that it is not important as an intermediate leading to principal product formation. Stevenson has found that toluene gives no evidence of molecule–ion reactions under conditions where they have been observed with related compounds.[20]

Ethylbenzene in the helium glow discharge gives products which differ only slightly from those formed from toluene (Table IV). Under similar conditions of discharge, ethylbenzene reacts more completely than

TABLE IV[a]

PRODUCTS FROM THE GLOW DISCHARGE OF ETHYLBENZENE

Low mol. wt., %	15	Recovery, %	80
Benzene, %	18	Ethylbenzene, %	68
Toluene, %	43		
Phenylacetylene, %	4		
Styrene, %	17		

[a] These percentages have the same significance as those reported in Table I.

toluene, with about the same degree of tar formation. Again, the absence of products which might have been expected is fully as intriguing as the ratios of the products that were formed. The appreciable amount of ethylbenzene formed from toluene would encourage the prediction of the formation of n-propyl- or isopropylbenzene from ethylbenzene. In fact, less than 1% of these compounds were present.

The reaction of o-xylene in helium formed benzene (13%), toluene (31%), ethylbenzene (8%), m- and p-xylene (5%) and 1-methyl-2-ethylbenzene (12%) as well as small amounts of other higher boiling materials. The extent of reaction was about the same as that for ethylbenzene. Both m- and p-xylene showed corresponding product distributions.

Benzene reacted less readily than the alkylbenzenes in the glow discharge (about 5%), to form 50% low molecular weight materials, 30% toluene, 5% ethylbenzene and 15% phenylacetylene. The formation of toluene as the major product requires a series of rather severe rearrangements. Schüler obtained similar products from an electrode discharge in benzene, together with a much higher formation of biaryl products.[21]

Cycloheptatriene and bicycloheptadiene have been shown to give cracking patterns similar to that obtained from toluene.[22] The products in glow discharge also show a likeness (Table V). A major difference in the mass spectrum of bicycloheptadiene is a peak assigned to cyclopentadiene. This is paralleled in the discharge reaction by the formation of 33% of cyclopentadiene.

A survey of the reactions of a substantial number of aromatic and aliphatic compounds allows certain generalizations about their behavior. Aromatic compounds react with from 5% to 60% conversion to give a small number of principal products. Aliphatic compounds react with 1–3% conversion to give many products. Among the aliphatic compounds tested were cyclohexane, tetramethylethylene, diethyl ether, n-hexyl acetate and 2-methylcyclohexanone. The aromatic compounds included alkylbenzenes and aromatic ethers, esters and halides; results with these compounds will be detailed in subsequent papers. A typical comparison is that of 2-octanone and aceto-

(20) D. P. Stevenson, private communication.

(21) H. Schüler, K. Prchal and E. Kloppenburg, Z. Naturforsch., 15a, 308 (1960).

(22) S. Meyerson, P. N. Rylander, J. Chem. Phys., 27, 901 (1957); S. Meyerson, J. D. McCollum and P. N. Rylander, J. Am. Chem. Soc., 83, 1401 (1961).
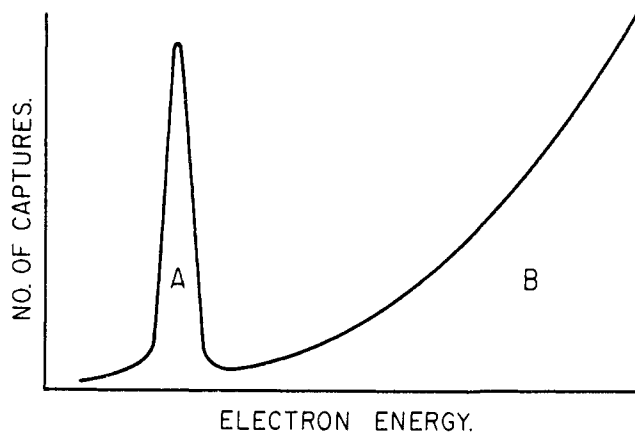
Fig. 2.—Illustration of a possible resonant electron capture.

phenone. Under approximately the same conditions, acetophenone reacts with 35% conversion to give three compounds which account for 95% of the product, whereas 2-octanone gives 3% reaction to form 16 products in approximately equal amounts. This order of reactivity is very different from that found in radiolysis experiments, where G-values for aliphatic compounds is often six times that for aromatic compounds.

The order of reactivity bears little relation to the ionization potential of the compound, a fact which makes the molecule-cation seem even less inviting as an intermediate. Tetramethylethylene, for example, with an ionization potential of 8.30 v.[23] reacted with about 3% conversion, whereas toluene with a larger ionization potential, 8.82 v.,[24] reacted with 10–20% conversion when a mixture of the two hydrocarbons was used.

The present results do not allow an equivocal selection of the method of energy transfer to the organic molecule. However, two possibilities which appeared most attractive at the start of this work, formation of

TABLE V[a]

PRODUCTS OF THE GLOW DISCHARGE OF CYCLOHEPTATRIENE
AND BICYCLOHEPTADIENE

	Cyclo-hepta-triene[b]	Bi-cyclo-hepta-diene[b]		Cyclo-hepta-triene[b]	Bi-cyclo-hepta-diene[b]
Low mol. wt.	8	11	Toluene	57	29
Cyclopenta-diene	—	33	Ethylbenzene	6	2
Benzene	20	9	Phenylacety-lene	2	1
Cyclohepta-triene	47	10			
Bicyclohepta-diene	—	55	Styrene	6	1

[a] Percentages have the same significance as those reported in Table I. [b] We thank Shell Chemical Co. for gifts of these hydrocarbons.

(23) W. C. Price and W. T. Tutte, Proc. Roy. Soc. (London), **A174**, 220 (1940).
(24) K. Watanabe, J. Chem. Phys., **22**, 1564 (1954).

radicals or of molecule cations, now appear to be relatively unimportant in product formation.

Two possible methods of energy transfer remain worthy of consideration: excitation by a photon or by near collision by an electron and electron capture to form an intermediate molecule anion.

Light of various frequencies certainly exists in the visible glow of a discharge, but the principal reactions we observe are apparently not due to photolyses. Ketones, for example, photolyze readily to produce radicals, yet 2-octanone is comparatively unreactive in our discharge (vide supra). Moreover, photolysis of toluene is reported to yield principally volatile gases and polymer.[25]

Electron capture to form intermediate anions remains as the only reasonable source of energy transfer to produce the principal products. This mechanism is consistent with the greater reactivities of compounds having extensive π-electron networks; such compounds appear to have higher electron affinities than their saturated counterparts. Moreover, this mechanism can explain the relative insensitivity of principal product ratios to electron energy. Electron capture to give the molecule anion is a resonance phenomenon, and the probability of capture depends directly on electron energy. A plot of number of captures against electron energy can have the general shape shown in Fig. 2.[26] The resonance peak at A corresponds to molecule-anion formation, whereas the gradual increase at B corresponds to fragmentation to form a neutral and a negative species, or negative, neutral and positive species accompanied by an electron.

Since the energies required for capture are low, a reasonable number of captures will always be present in the discharge. An organic molecule can then be activated to about the same extent by capturing an electron of a particular energy, and would react to give a product composition characteristic of the energy absorbed rather than of the total energy available. As the average energy of the electrons increases, more molecules will be fragmented (B portion of the curve) and these fragments may well lead to tars and noncondensables. Direct ionization to give molecule cations may also give these products at higher electron energy.

This conclusion must remain tentative until pending additional results; nevertheless, this introductory study has demonstrated that microwave glow discharge provides a means of effecting novel organic reactions. We are continuing our studies with applications to additional structures and by following the course of specific isotope labels.

(25) R. R. Hentz and M. Burton, J. Am. Chem. Soc., **73**, 532 (1951).
(26) An explanation of this phenomenon and a sample curve of this sort is given in F. H. Field and J. L. Franklin, "Electron Impact Phenomena," Academic Press, Inc., New York, N. Y., 1957, p. 25.