The Dissociation of Toluene Vapor in a Radiofrequency Discharge

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The emission spectra resulting from the excitation of toluene vapor in electrode discharges have been investigated by Schuler as a part of his extensive work dealing with the behavior of molecules in discharges.(1) He found that two distinctly different spectra were emitted. One, the normal toluene emission spectrum, was centered in the 2600-3000 A° region and was related to the forbidden benzenoid absorption band of toluene in the crude minor image relationship which characterizes fluorescence emission. This spectrum, as it was obtained in the present study, is shown in figure 1. In addition to this ultraviolet emission, Schuler also observed a visible emission spectrum from toluene which appeared in the 4300 to 5000 A° region, the details of which were not published. This spectrum was designated the "blue spectrum" and was assigned to the benzyl radical without strong supporting evidence.

In a subsequent study of the reactions of toluene vapor in a high voltage electrode discharge, Kraaijveld and Waterman(2) investigated the formation of the bibenzyl molecule fror toluene and found that, under optimum conditions in a 2400 V arc, 40% of the toluene vapor could be converted to bibenzyl. The other products formed under these conditions were not investigated. This result, as well as those obtained by Schuler, imply the existence of benzyl radicals as the major species present in electrode induced toluene discharges.

More recently, Streitwieser and Ward conducted the first comprehensive study which was concerned with the range of products formed from the electrodeless microwave excitation of toluene vapor.(3) In this study, flowing toluene vapor in a helium carrier gas stream was excited by a 3 KMc microwave generator, The spectrum of the light emitted was not investigated, however the products were carefully determined. The composition of the mixture of products obtained is shown in figure 2.

The very minor amounts of dimer biaryls which were formed in this discharge suggested that radical intermediated were not of dominant importance. The lack of formation of the xylene isomers was also interpreted as supporting the absence of methyl radicals in the plasma.

Two other possibilities, the molecular cation and anion were considered as likely intermediates in the microwave discharge. Results obtained from labeling experiments ruled out consideration of the cation, and it was tentatively concluded that anion intermediates remained as the most likely possibility.

This result contrasted interestingly with the conclusions which had been previously drawn regarding the dominance of radicals in toluene discharges and cast some doubt on these conclusions. However, work which had been done in W. D. Cooke's laboratory at Cornell University suggested that very significant differences might be anticipated between the products resulting from the excitation of organic vapors in a microwave powered discharge and the excitation of these vapors with a radiofrequency source. It was, therefore, decided to investigate both the spectra and the products obtained when toluene vapor was excited in a 28 Mc. radiofrequency discharge.

The apparatus used in this study is shown in block diagram form in figure 3. Flowing toluene vapor was passed through a discharge powered by an R.F. transmitter operating at 28 megacycles and 100 watts output. The pressure of the vapor was maintained constant at 0.10 to 0.15 mm. Materials formed in the plasma were collected in traps maintained at 0° and 80° and were subsequently investigated by gas chromatographic and spectroscopic techniques. The light emitted from the discharge was focused into a scanning monochromator and detected by a IP-28 photomultiplier tube. The amplified output of the photomultiplier was recorded electronically. Under the conditions used in these experiments, toluene was converted to products in 12 to 16% yield with 75 to 82% of the toluene being recovered unchanged.

TOLUENE ULTRAVIOLET EMISSION

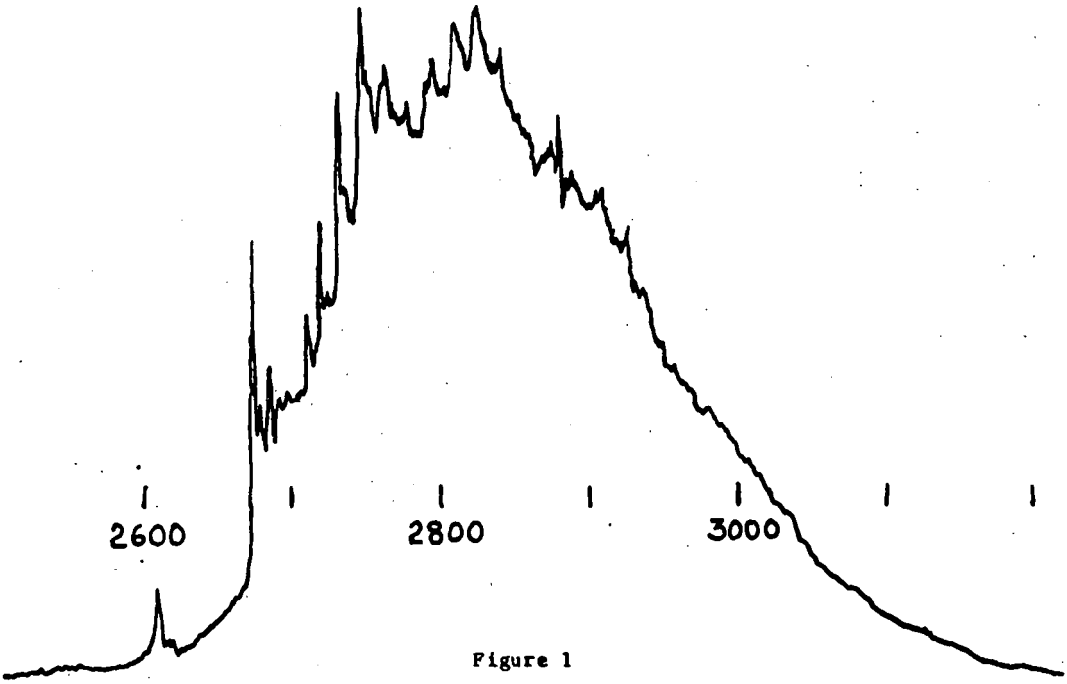


Figure 1

PRODUCTS FROM TOLUENE VAPOR
IN A 3 KMc. POWERED DISCHARGE

	%
BENZENE	49
ETHYLBENZENE	30
PHENYLACETYLENE	8
STYRENE	3
XYLENE ISOMERS	TRACE
BIBENZYL	~0.5
DIPHENYLMETHANE	~0.2
BIPHENYL	~0.1

Figure 2

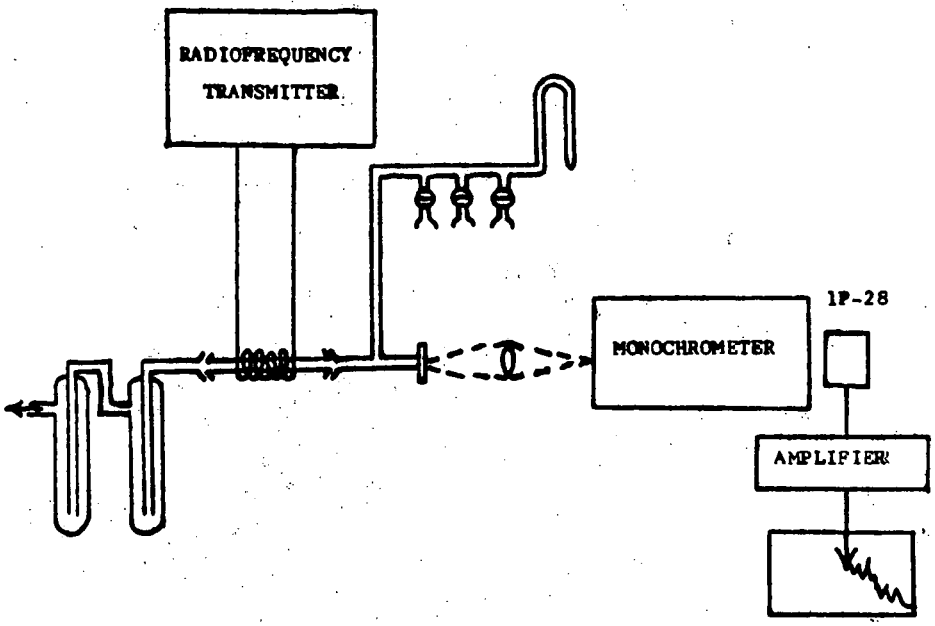


Figure 3

PRODUCTS FROM A 28 MC. DISCHARGE IN TOLUENE

PRODUCT	%
BENZENE	35
ETHYLBENZENE	41
BIBENZYL	16
DIPHENYLMETHANE	7
BIPHENYL	2
XYLENE ISOMERS	<1

Figure 4

A summary of the products formed in the R. F. powered discharge is presented in figure 4. It should be noted that these results are normalized to exclude recovered toluene, non-condensable gases and polymeric materials which in combination accounted for 3 to 6% of the original toluene vapor.

The formation of substantial amounts of dimer biaryls; bibenzyl, diphenylmethane and biphenyl is of particular significance since, as noted above, the formation of only trace amounts of dimer biaryls was observed in the microwave discharge. Additional experiments were conducted in which a helium carrier gas was used, and no substantial difference in the nature and amounts of products formed was noted. The change in product ratios, therefore, appears to reflect a change in mechanism which results from the use of an R. F. powered discharge.

The products formed in this study, in particular the large amounts of biaryls, indicate that free radicals are the major intermediates leading to the formation of products. The compounds formed can be readily explained by the series of radical combination and hydrogen abstraction reactions involving benzyl, phenyl and methyl radicals which are outlined in figure 5.

It should be noted that minor, but definite amounts of the three xylene isomers were formed in the radiofrequency discharge. The trace amounts of these isomers which were formed from the dissociation of toluene vapor in a microwave powered discharge has previously been used as an argument against the presence of methyl radicals in the microwave discharge.[3] As is shown in figure 6, however, it has been demonstrated that methyl radicals react with toluene vapor with a hundred fold preference for the side chain rather than the ring positions.[4] It is, therefore, entirely consistent with the presence of methyl radicals in the R. F. discharge that reaction should take place predominantly with the toluene side chain to form ethylbenzene rather than with the ring positions to yield xylene isomers, although the formation of small amounts of xylene should be anticipated.

Experiments in which specifically labeled deuteriotoluene was passed through the R.F. discharge afforded additional experimental data which supported the importance of radical intermediates. The products formed from the labeled toluene were collected, separated by chromatographic techniques, and the distribution of the deuterium label determined by infrared and nuclear magnetic resonance spectroscopy and mass spectrometry.

The side chain of the recovered ethylbenzene was found to be heavily deuterated. The partial mass spectrum of the recovered ethylbenzene compared to the mass spectrum of un-deuterated material is shown in figure 7. The parent peak of the recovered material is five mass units higher than the corresponding peak in the un-deuterated material, and demonstrates the inclusion of five deuterium atoms in the molecule. The base peak of the unlabeled ethylbenzene molecule results from a P-15 cleavage corresponding to the loss of a methyl group. In the spectrum of the recovered material, the base peak results from P-18 cleavage and clearly demonstrates the methyl group of the side chain to be fully deuterated. This molecule presumably forms from the combination of $C_7H_5D_2$ radical with a CD_3 radical.

The distribution of the deuterium label in the benzyl fragment can be demonstrated by considering the NMR spectrum of the recovered bibenzyl. In figure 8, the 100 Mc. proton magnetic reasonance spectrum of un-deutered bibenzyl and that of the recovered material are compared. It is important to note that the 5:2 ratio of aromatic to methylene protons observed in the non-deuterated material would also be observed with the partially deuterated molecule if the deuterium label were uniformly distributed. The greatly reduced methylene proton peak in the spectrum of the recovered material, however, clearly demonstrates that the label remains localized in the side chain of the benzyl fragment, and is not distributed throughout the ring.

This result is entirely consistent with the presence of free radical intermediates in the discharge since, as is shown in figure 9, it has been demonstrated that the un=ionized benzyl radical does not undergo any type of rearrangement which would result in the randomization of a label, such as the formation of the tropylium radical.[5] By contrast, the benzyl cation does undergo an immediate arrangement to the tropylium ion, which would result in uniform distribution of the deuterium label.[6] Since this is not observed, the benzyl cation can be ruled out as a

PRODUCT FORMATION REACTIONS

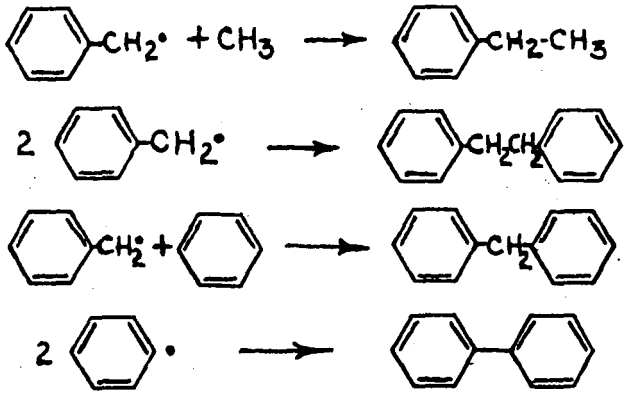
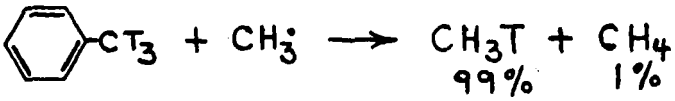


Figure 5

REACTION OF METHYL RADICALS WITH TRITIATED TOLUENE



	RELATIVE RATE CONSTANTS AT 85°
o-	0.76
m-	0.26
p-	1.00
CH_3-	156

I.V. BEREZIN, et. al., ZHUR. OBSCHEI KHIM., 30, 4093 (1960). C.A., 55, 27153 b.

Figure 6

PARTIAL MASS SPECTRA OF ETHYL BENZENE

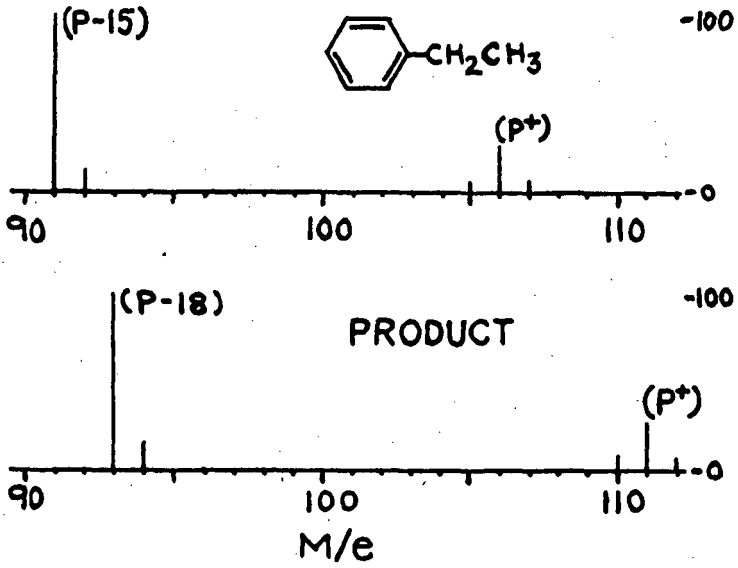


Figure 7

PARTIAL NMR SPECTRA OF BIBENZYL

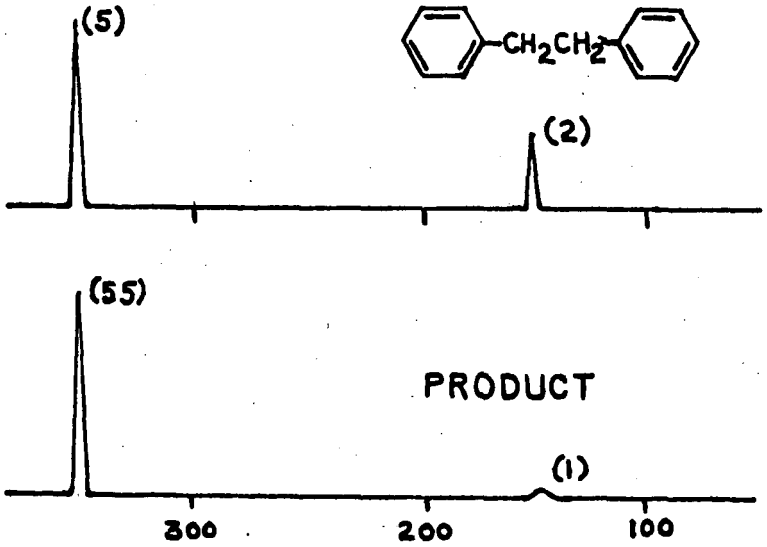


Figure 8

BENZYL CATION AND RADICAL BEHAVIOR

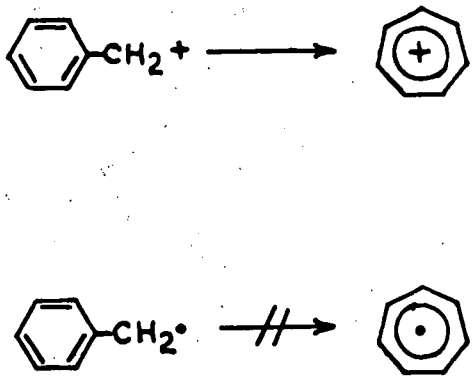


Figure 9

PRODUCTS FROM IODINE AND TOLUENE VAPOR IN A 28Mc. DISCHARGE

PRODUCT	%
BENZYL IODIDE	47
IODOBENZENE	14
ETHYLBENZENE	11
BENZENE	13
METHYL IODIDE	6
UNIDENTIFIED	9

Figure 10

significant reaction intermediate.

Additional experiments were conducted in which toluene and iodine vapors were passed through the R.F. discharge together. Figure 10 shows the composition of the products formed in this experiment. In view of the known affinity of iodine for free radicals, (7) the formation of benzyl iodide, iodobenzene and methyl iodide together with greatly reduced amounts of the previously observed products argues for the presence of benzyl, phenyl and methyl radicals in the discharge.

It should also be noted that the visible emission spectrum which is shown in figure 11 was observed with the toluene discharge. This spectrum is similar to that which Schuler had previously observed from electrode toluene discharges and assigned to the benzyl radical.

In summary, the different products and intermediates formed in this work as contrasted to Streitwieser and Ward's study indicates that significant differences are to be anticipated between R.F. and microwave powered discharges, and unequivocally establish the importance of radical intermediates in the toluene R.F. discharge. Additionally, the hazards involved in the generalization of data obtained in a specific type of discharge are readily apparent from these observations.

Literature Cited

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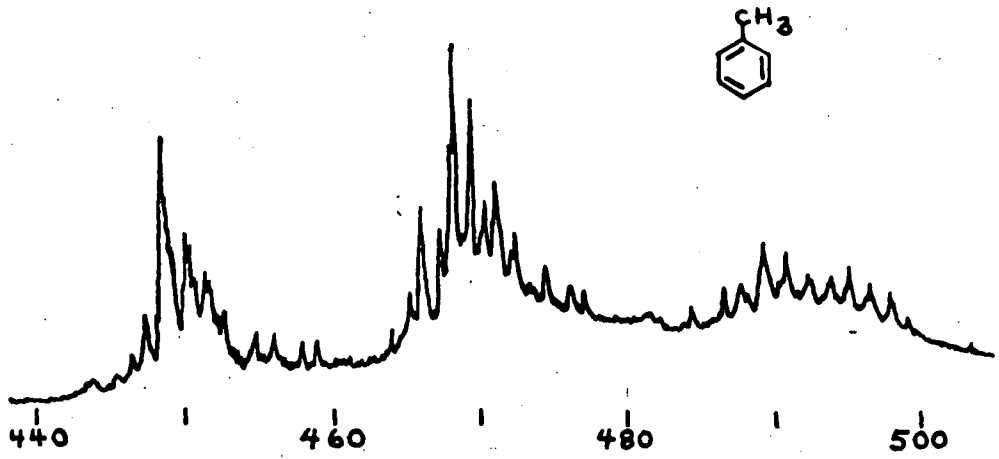

Figure 11

Toluene Visible Emission