Dynamics and Mechanism of the Plasmolysis of Anisole

Meguru Tezuka and Larry L. Miller*

Contribution from the Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455. Received November 16, 1977

Abstract: The reaction of anisole (1) in the plasma produced by a 13.6-MHz radio frequency generator has been studied. Typical conditions are a flow rate, r, of 1 mmol/min at 30 W of applied power, P. The major products are o- and p-cresol, phenol, and ethane. It is found that $-\log (1)/(1_0) = 0.021\ Pr^{-1} + 0.05$ where $(1)/(1_0)$ is the fraction of anisole recovered in one experiment. This rate law is consistent with rate-limiting, electron-impact activation. The number and energy of the electrons, therefore, are important in determining the rate and these in turn depend upon the pressure of organic material in the reactor. The ratio of cresols to phenol is constant if the conditions are such that <60% of the anisole reacts. This is consistent with both products being formed in reactions which are first order in anisole. Plasmolysis of mixtures was performed. Argon had no effect on the anisole rate or products even when present in excess. Organic additives present in a mole fraction ranging from 0.1 to 0.7 gave rate data for disappearance of anisole consistent with the above rate law where r is the total flow rate of organic. The relative reactivities of the organic additives $[\log (\text{add})/(\text{add}_0)]/\log[(1)/(1_0)]$ are as follows: nonane, 0.11; benzonitrile, 0.25; tripropylamine, 0.26; cumene, 0.33; benzene, 0.30; benzaldehyde, 1.55. The reaction of anisole in the presence of benzene produced toluene at the expense of cresols. The reaction products of o-, m-, and p-anisole-d_1 and methoxyanisole-d_3 were studied. The results are interpreted in terms of a process involving cleavage recombination via methyl radicals. A minor pathway is also revealed by the labeling studies.

This study concerns reactions in the plasma of a radio frequency (rf) discharge. The plasma chemistry of atoms and diatomic molecules has received extensive attention,[1] but very little is known about the behavior of organic compounds under these conditions. The experiment involves distillation of an organic compound through a glass tube. An rf generator supplies energy to the contents of the tube, initiating reactions, and the products are collected in a cold trap. Although the technique promises to be preparatively useful, it is, at present, difficult to predict reactivity or to manipulate conditions so that desirable products can be obtained. Characterization of plasmolysis dynamics and mechanisms is crucial to improving this situation and we present here some results on these aspects.

The plasmolysis of anisole (1) was chosen for study. Suhr and Weiss[2,3] have previously investigated this reaction and found the major products to be o-cresol (2), p-cresol (3), and phenol (4). m-Cresol, benzene, toluene, methylcresols, and
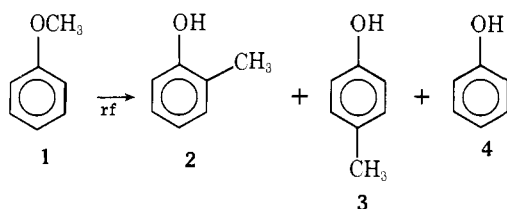
methylcyclopentadiene were present in 0–3% yield. A number of aryl ethers and alkyl anilines were shown to react similarly. The isomerization to form o,p-cresol is a simple, yet unique reaction and some effort has already been made to elucidate its mechanism. The existing hypotheses involve ions. A pathway which accounted for all the results used anisole cation radical ($1^{+}\cdot$) as initiator of a chain process (Scheme I). The propagation step in this chain was proposed to be reaction of phenoxonium ion 5 with 1. This proposal was based on the virtual absence of m-cresol and methylcresols, the pressure dependence of product ratios, the intermolecular nature of the isomerization, and analogies to mass spectrometry. This is one of the most thorough studies existing and the anisole reaction provided an attractive example for the dynamics and trapping investigations we wished to undertake. We were especially intrigued by the proposed ionic mechanism. The possibility of doing preparative-scale, ionic chemistry in the gas phase is one of the most fascinating aspects of plasma chemistry. Although ions are obviously present in any plasma, it is not clear that they are precursors of the major products.

Scheme I
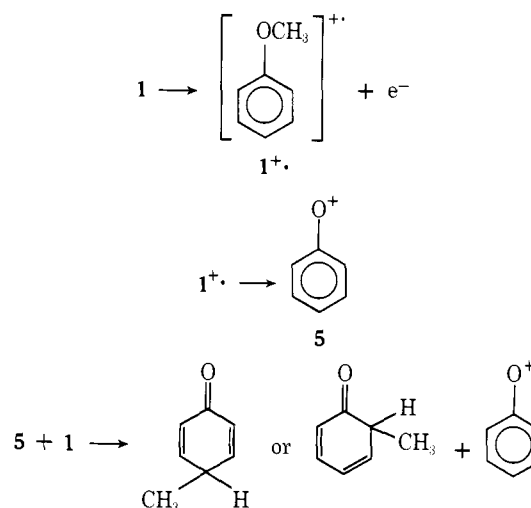
A primary concern of the present study is analysis of the products of anisole plasmolysis as flow rate (r) or applied power (P) are varied and various additives are included in the reactant stream. These dynamics results are introduced into a kinetic treatment and then the mechanism is treated. In addition to the rate data, results from isotopic labeling and trapping experiments are reported.

Results and Discussion

Initial studies were performed using a previously described apparatus (apparatus A),[4] designed to keep the flow of reactant steady and ensure reproducible results. Later, attention was focused on studies in which two compounds were simultaneously reacted and a slightly different apparatus (apparatus B, schematically shown in Figure 1) was constructed, which had dual reactant reservoirs. This allowed the flow rates of two compounds to be independently controlled. When the reaction of anisole alone was carried out in apparatus B, one of the reactant reservoirs was replaced with a stopper.

In each run the flow rate, r, the applied power, P, and the product composition were measured. Details are given in the Experimental Section. For several runs the pressure at entrance to the reactor was measured before applying power. Although it would be of interest to measure the pressure during plas-
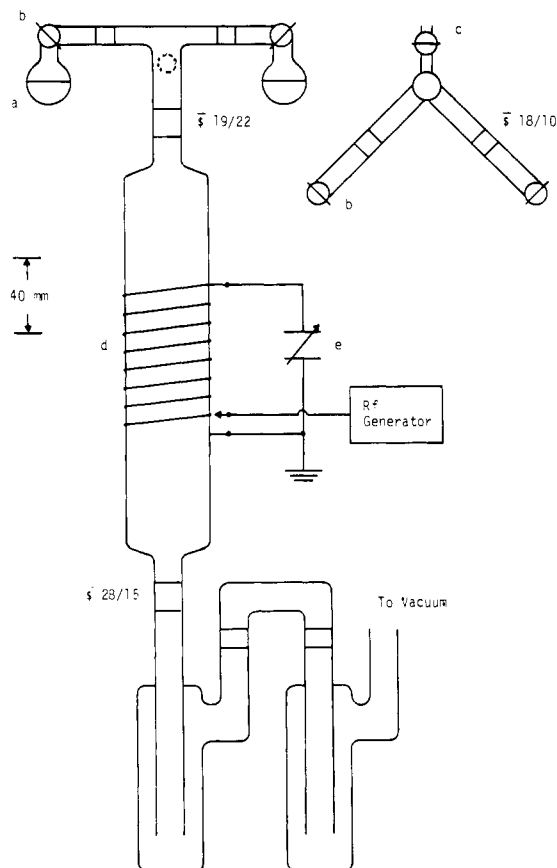
Figure 1. Scale drawing of apparatus B: a, reactant vessels; b, Teflon needle valve; c, valve to pressure gauge; d, $^1/_8$-in. copper tubing; e, variable air capacitor.

Table I. Plasmolysis of Anisole

Run	P, W	$r_1.^a$ mmol/min	Products, % yield^b			
			1	**2**	**3**	**4**
Apparatus A						
1	5	3.09	94.6	1.2	tr	1.4
2	15	1.69	69.7	8.6	3.6	6.6
3	30	0.50	13.2	5.3	2.7	11.1
4	30	1.09	33.3	12.1	5.1	15.9
5	30	2.03	55.4	11.9	4.8	8.9
6	30	5.94	85.6	4.8	1.9	2.6
7	50	1.09	28.0	5.3	3.7	15.8
8	50	2.44	44.1	14.9	6.2	14.2
Apparatus B						
9	10	1.07	52.5	11.7	6.0	10.8
10	10	1.41	59.3	10.5	5.9	8.8
11	20	1.25	36.7	14.0	7.6	14.0
12	20	1.40	40.5	14.0	7.7	12.8
13	20	2.08	56.7	12.2	6.9	8.6
14	30	0.77	13.8	11.5	7.0	18.0
15	30	1.04	20.1	12.3	7.3	17.0
16	30	1.62	32.5	14.2	8.6	15.0
17	30	2.19	51.1	13.4	7.8	9.6
18	30	2.61	57.0	12.6	7.5	8.2
19	40	1.73	35.1	13.2	7.3	14.9
20	40	2.08	56.7	12.2	6.9	8.6
21^c	30	0.36	9.4	2.3	1.5	6.2
22^c	30	0.96	23.7	10.9	6.5	17.4
23^c	30	1.60	40.7	13.1	7.9	13.5

^{a} Flow rate of anisole. ^{b} Yield based on moles of anisole passed through plasma. ^{c} Argon was used as an additive at total pressure of ~0.2 Torr.

molysis this is experimentally difficult and interpretation may not be simple because of pressure gradients in the reactor. The flow rate is, however, easy to measure and initial interpretations are simpler because it is both temporally and spatially averaged.

Qualitatively it is found that the extent of conversion (the rate of reaction) depends on both r and P. Low power or high flow rate gives low conversion. This is true for many compounds. Arguments are developed below which relate the quantitative variation in rate to variations in the number and energy of the electrons in the plasma.

The product mixture from anisole in the presence and absence of additives was qualitatively similar in all the runs. As reported previously,[2,3] o-cresol, p-cresol, and phenol are obtained as major products. If r and P are such that the conversion of anisole is <60% the *relative* yields of the products **2, 3**, and **4** are constant. Under conditions causing more conversion the ortho/para ratio, **2/3**, still remains constant at 1.8 ± 0.1, but greater relative yields of phenol are found. Under these conditions the products are themselves reactive and overconversion becomes significant.[5] In some experiments, gaseous products were analyzed as well as liquid products. Ethane was the major component, together with some ethylene, acetylene, and a trace of propane. In every case, the number of moles of C_2 compounds were found to be more than half of the number of moles of phenol. Methane was not detected, but is too volatile to trap under these conditions. Benzaldehyde, dimethylphenol, phenetol, biphenyl, phenyl ether, and dibenzofuran were detected as minor products in addition to those reported previously. However, the yields were generally only 1 or 2%. Finally, polymer was formed as a thin film inside the reaction chamber. This is especially prevalent at low flow rate.

Kinetics of Anisole Plasmolysis. The percent yield of **1** from

Table I expresses the fraction of anisole recovered, $(1)/(1_0)$, in any particular run. We wish to interpret the dependence of $(1)/(1_0)$ on P and r. This quantitative interpretation derives from the accepted mechanism for sustaining a discharge.[6] In this mechanism the rf field accelerates the few free electrons in the gas and by electron impact these cause further ionization until a steady state is reached. The resulting plasma is a nonequilibrium mixture in which the electrons have a relatively high temperature (kinetic energy), but the neutrals are near ambient. It may be speculated from other studies that the degree of ionization is low (~5 × 10^{11} electrons/cm^3) and that the electron energies should have an approximately Maxwellian distribution with a mean energy of a few electron volts. It is generally accepted that organic molecules which pass through the discharge region are primarily activated by electron impact. The rate of reaction and the type of reaction products will, therefore, depend on the number and energy of the electrons, the electron energy function, $f(\epsilon)$.[6]

Assuming that the rate-determining step is impact of a suitably energetic electron on anisole, the following integrated rate equation can be written

$$-\ln (p_1/p_1^0) = k_1 \tau f(\epsilon) \tag{1}$$

where τ is the residence time in the plasma, p_1^0 is the pressure of **1** at entrance into the plasma, and p_1 is the anisole pressure at exit from the plasma zone. Thus p_1/p_1^0 can be equated to the fraction of **1** recovered $(1)/(1_0)$. Note that there are two parts to the right-hand side of this equation: a pseudo-first-order rate equation for electron-impact activation of anisole, and $f(\epsilon)$ which expresses the dependence of rate on the number of electrons and the electron energy distribution. This part can be used to describe the effect of varying P, r, or p on the rate.[7] The precise form of the dependence of k on these experimental variables is, however, not known and may be complex. We have, therefore, sought an empirical correlation based upon the premises that (1) increasing P should increase the applied
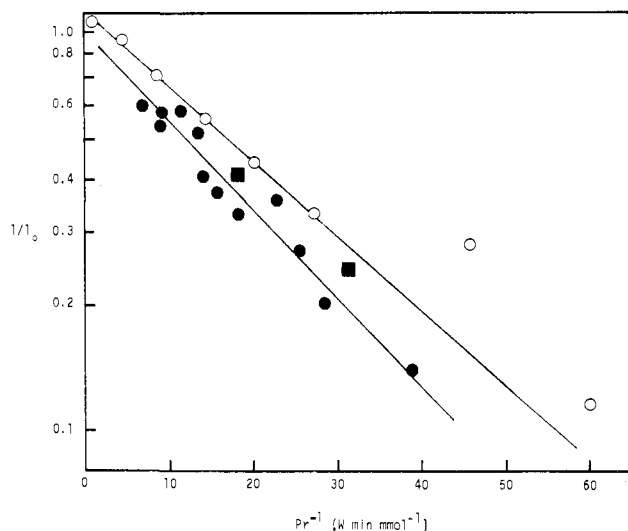
Figure 2. Kinetics of anisole plasmolysis: O, apparatus A; ●, apparatus B; ■, apparatus B, argon added.

field and therefore the electron energies and/or their number and (2) increases in p should lead to a cooler plasma because the electrons will transfer more of their energy to the molecules. We will assume that over the range of P, p studied there is a direct dependence of $f(\epsilon)$ on P/p. Therefore

$$-\ln [(\mathbf{1})/(\mathbf{1})_0] = k'\tau P/p \qquad (2)$$

where k' includes all the proportionality constants. Assuming the ideal gas law

$$\tau/p = V/RTr$$

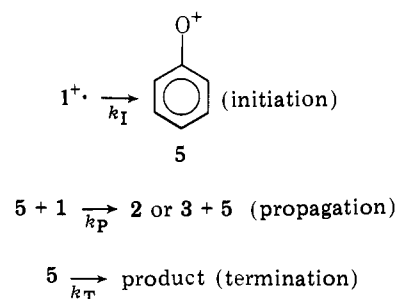$$-\ln [(\mathbf{1})/(\mathbf{1})_0] = k'VP/RTr \qquad (3)$$

Comparison of theory with experiment is shown in the semilog plot, Figure 2. The least-squares line is $-\log [(\mathbf{1})/(\mathbf{1}_0)] = 0.021$ $Pr^{-1} + 0.05$ with apparatus B. It is, therefore, indicated that electron impact on anisole is the rate-limiting step. Indeed, although the form of $f(\epsilon)$ may not be applicable over a wider range of Pr^{-1}, it is highly unlikely that a different rate law for anisole disappearance would produce a satisfactory fit and still retain any kinetic rationality. Several have been tested, including a "second-order" rate law (eq 4) and found to be unsatisfactory.

$$\{[(\mathbf{1}) - (\mathbf{1}_0)]/(\mathbf{1})\}/(\mathbf{1}_0) = -k'' Pr^{-1} \qquad (4)$$

The observed rate law is surprisingly simple when one considers the variety of species and energy transfer modes which could be involved. Two important aspects of the dynamics situation should be noted. In each run the circuit is independently balanced to give zero reflected power. The circuit tuned for one pressure is not perfectly tuned for another. This tuning has been recently shown to provide a means of estimating the average electron density in the plasma[9] and future kinetic studies will attempt to utilize the data which it provides. Second, the pressure which appears in eq 2 must be considered the average pressure in the plasma zone. Not only are there pressure gradients in this zone but, because the composition changes as reaction takes place, it is actually assumed above that the average pressure of organic compounds (reactant and products) determines $f(\epsilon)$. This assumption is justified by the kinetic data obtained from experiments with additives.

Although we do not have good $p_1{}^0$ measurements, the available numbers indicate that below $r = 1.5$ mmol/min, $p_1{}^0$ is proportional to r so that in this region τ is constant at ~0.1 s. Above this r value τ varies substantially. It is an important facet of this approach that the temporally and spatially aver-

Scheme II

$$\mathbf{5} + \mathbf{1} \xrightarrow{k_\mathrm{P}} \mathbf{2} \text{ or } \mathbf{3} + \mathbf{5} \quad \text{(propagation)}$$

$$\mathbf{5} \xrightarrow{k_\mathrm{T}} \text{product (termination)}$$

aged rate equation (3) can account for the data under both conditions. A certain advantage of this approach is that it requires only simple measurements which can be made accurately.

A comparison of results obtained using the two different reactors is of interest. It is found expectedly that the extent of conversion is slightly different in the two reactors, but the form of the rate law is unchanged.

These kinetic data do rule out some possible schemes. Consider in particular the chain process in Scheme II. The rate equations are

$$-\,\mathrm{d}(\mathbf{1})/\mathrm{d}t = k_\mathrm{I}(\mathbf{1}) + k_\mathrm{P}(\mathbf{1})(\mathbf{6})$$

$$\mathrm{d}(\mathbf{6})/\mathrm{d}t = k_\mathrm{I}(\mathbf{1}) - k_\mathrm{T}(\mathbf{6})$$

A steady-state assumption gives

$$(\mathbf{5}) = k_\mathrm{I}(\mathbf{1})/k_\mathrm{T}$$

$$-\,\mathrm{d}(\mathbf{1})/\mathrm{d}t = k_\mathrm{I}(\mathbf{1}) + k_\mathrm{I}k_\mathrm{P}(\mathbf{1})^2/k_\mathrm{T}$$

If this is a chain process

$$k_\mathrm{P}(\mathbf{1}) \gg k_\mathrm{T}$$

$$\mathrm{d}(\mathbf{1})/\mathrm{d}t = k_\mathrm{I}k_\mathrm{P}(\mathbf{1})^2/k_t$$

The reaction is second order in **1**. It is, therefore, ruled out.

Similarly, one can rule out schemes of the following type in which the rate-limiting step (rls) is attack of an excited, or ionized, or fragmented anisole (A*) on another anisole molecule.

$$\mathbf{1} + \mathrm{e}^- \rightarrow \mathrm{A}^* + \mathrm{e}^-$$

$$\mathrm{A}^* + \mathbf{1} \xrightarrow{\text{rls}} \text{products}$$
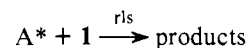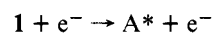
Now that the kinetics of anisole disappearance has been established, one comes to discuss the kinetics for each product, too. Assuming that formation of both phenol and the cresols follows a first-order rate equation with respect to anisole:

$$\mathrm{d}(p_{2+3})/\mathrm{d}t = k_2 f(\epsilon)p_1 \qquad (5)$$

$$\mathrm{d}(p_4)/\mathrm{d}t = k_3 f(\epsilon)p_1 \qquad (6)$$

Where p_{2+3} and p_4 are pressures of $(\mathbf{2} + \mathbf{3})$ and **4** at exit from the plasma zone. Integrating eq 5 and 6, one can derive the following equations

$$(\mathbf{1})/(\mathbf{1}_0) = 1 - \frac{k_1}{k_2}\left[\frac{(\mathbf{2} + \mathbf{3})}{(\mathbf{1}_0)}\right] \qquad (7)$$

$$(\mathbf{1})/(\mathbf{1}_0) = 1 - \frac{k_1}{k_3}\left[\frac{(\mathbf{4})}{(\mathbf{1}_0)}\right] \qquad (8)$$

showing the relationship between anisole recovery, $(\mathbf{1})/(\mathbf{1}_0)$, and product yields $(\mathbf{2} + \mathbf{3})/(\mathbf{1}_0)$ and $(\mathbf{4})/(\mathbf{1}_0)$. As seen in Figures 3 and 4, the plots according to eq 7 and 8, respectively, exhibited the linear relationships with good correlation. The deviation from solid lines, which is conspicuous for anisole
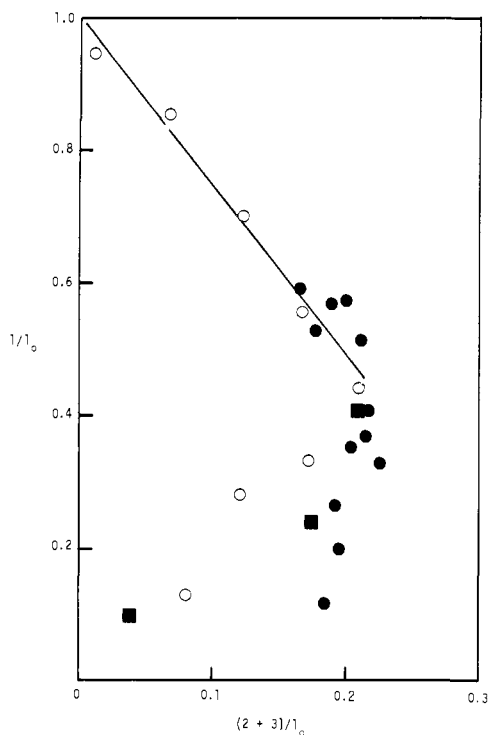
Figure 3. Kinetics of cresol formation: O, apparatus A; ●, apparatus B; ■, apparatus B, argon added.

Figure 4. Kinetics of phenol formation: O, apparatus A; ●, apparatus B; ■, apparatus B, argon added.

conversions over $\sim$60% in Figure 3 and over $\sim$80% in Figure 4, is attributed to the further plasmolysis of cresol and phenol. This demonstrates that the formation of phenol and cresols has the same dependence on the anisole partial pressure. Schemes like Scheme III are improbable. In such mechanisms an excited or ionized anisole (A*) decomposes unimolecularly to give phenol or attacks unexcited **1** in a competitive reaction. Such schemes should show preferential formation of cresol at higher flow rate.

Scheme III

$$1 + e^- \rightarrow A*$$

$$A* \rightarrow 4$$

$$A* + 1 \rightarrow 2 + 3$$
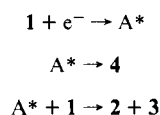
The effects of the two different reactors on the plasmolysis kinetics has been pointed out in Figure 2. There is, however, little difference on the products even in the regions of over-conversion. In Figure 4 the lines from a least-squares treatment are essentially identical. Insufficient data are available to get a least-square line with apparatus B in Figure 3.

Plasmolysis with Additives. It should be an interesting and useful mechanistic probe to examine the effects of additives on plasma reactions. Additions might change the reaction rate and product distribution, or result in crossover products. In addition, the additive experiments will give practical information about relative reactivities. Therefore, the plasmolyses of anisole with argon and with various organic additives were carried out using the dual reservoir reactor (apparatus B). As additives, nonane, benzaldehyde, tripropylamine, benzonitrile, cumene, benzene, biphenyl, naphthalene, phenylacetylene, aniline, piperylene, carbon tetrachloride, hexafluorobenzene, and anthracene were examined. When the ratio of additive to anisole (r_{add}/r_{1_0}) was <0.1, no effect on the anisole rate of reaction or products could be detected with an additive. However, when the flow rate of additive was increased to be comparable with that of anisole, several interesting results were obtained (Tables II and III).
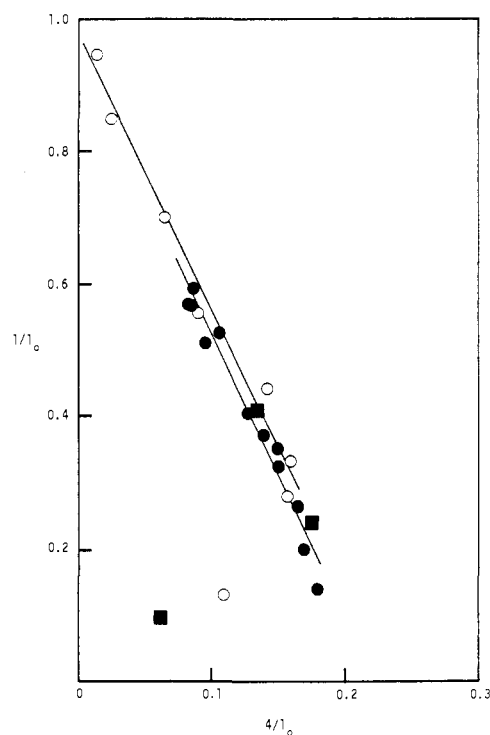
Data for runs made with argon show that the added gas (0.2 Torr) is essentially inert (Table I). Thus, the rate and the product yields of cresols and phenol are those predicted from the flow rate of anisole in the absence of argon (Figures 2–4). It is important to note that the gas is present in excess so that the total pressure is relatively high. Similar behavior was previously noted for the 2-butene reaction.[4] It is not unexpected since argon metastables (11.7 eV) and ions (15.8 eV) are much higher in energy than available excited states and ionic states of anisole. Argon also has no vibrational or rotational states and has been shown to be very ineffective at scattering low energy electrons. In a crude sense one can say that under these conditions one has an "anisole plasma" and that argon is an inert diluent.

The data with regard to organic additives are plotted in Figure 5. The line shown there is the least-square line from Figure 2. In contrast to the noninvolvement of argon, these additives act kinetically to cool the plasma in the same way as anisole. Thus, Figure 5 shows that the rate of reaction of anisole can be correlated with the total flow rate of organic (r_T). It does not correlate with r_1. This result is fully consistent with the discussion in the previous section, where $f(\epsilon)$ is determined by the total pressure of organic. We note again that the circuit is tuned to zero reflected power in each experiment.

Tripropylamine, nonane, benzonitrile, and cumene showed virtually no effect on cresol yields. Although they are not inert these compounds can be considered diluents and, thus, the product ratios test the mechanistic schemes. Consider Scheme III again where phenol formation is first order in anisole and cresol second order in anisole. In this case dilution with additive should give lower relative yields of cresol. It does not. This result again demonstrates that the formation of cresols and phenols have the same dependence on anisole partial pressure.

Data from reactions with benzene and benzaldehyde additives deviated significantly from the results with anisole above. The deviation depends on the ratio of benzene or benzaldehyde to anisole. Thus, as seen in Table III, as the ratio rises, the cresol yields fall, while yields of phenol and toluene show a

Table II. Plasmolysis of Anisole with Additives. I[a]

Run	r_1,[b] mmol/min	r_{add},[c] mmol/min	Products, % yield[d] 1	2	3	4	Recovd additive, %
			Nonane				
24	0.341	0.575	17.5	11.4	7.9	25.3	76.5
25	0.371	0.999	30.0	10.7	4.1	14.1	96.8
26	0.625	0.663	30.5	13.0	6.1	14.0	93.7
27	0.902	0.438	25.4	13.3	6.7	15.4	84.7
			Benzonitrile				
28	0.305	0.799	27.3	17.9	4.4	2.4	73.0
29	0.336	0.377	11.1	17.9	5.6	3.5	59.8
30	0.589	0.180	12.7	17.9	10.1	6.1	61.3
31	0.605	0.362	18.0	19.2	9.5	6.2	63.0
			Tripropylamine				
32	0.363	0.813	29.8	12.2	4.2	20.9	85.5
33	0.480	0.219	13.3	12.6	6.1	20.3	38.6
34	0.522	0.380	23.6	15.1	7.0	22.0	62.0
35	0.532	0.745	27.0	15.2	6.2	20.0	75.9
36	0.549	0.480	25.0	15.2	7.2	20.4	68.9
37	0.739	0.317	24.5	13.6	8.4	18.0	75.0
			Cumene				
38	0.288	0.628	37.1	11.1	5.3	18.3	71.8
39	0.420	0.540	36.5	11.3	5.7	16.7	74.3
40	0.597	0.404	34.6	13.6	8.1	17.1	71.4
41	0.638	0.595	42.9	12.9	6.5	17.3	72.8

[a] All runs at 30 W. [b] Flow rate of anisole. [c] Flow rate of additives. [d] Based on moles of anisole passed through plasma.

Table III. Plasmolysis of Anisole with Additives. 11[a]

Run	r_1,[b] mmol/min	r_{add},[c] mmol/min	Products, % yield[d] 1	2	3	4	Toluene	Recovd additive, %
			Benzene					
42	0.503	1.51	43.1	6.5	tr	18.6	10.9	83.5
43	0.869	1.34	52.7	7.9	2.8	15.4	5.2	81.3
44	0.893	0.084	21.2	12.1	6.6	18.7	tr.	56.0
45	1.19	0.917	49.8	10.6	4.5	13.9	2.7	80.9
			Benzaldehyde					
46	0.557	0.698	31.8	5.7	3.5	21.6	8.3	33.6
47	0.626	1.84	57.1	1.9	1.4	17.8	9.7	47.1
48	0.956	0.396	40.1	8.8	5.4	17.9	4.4	21.0
49	0.967	0.615	48.7	7.2	4.8	16.9	6.2	32.2

[a-d] Same as Table 1I.

quantitatively corresponding increase. (For example, see runs 17, 42, 43 and 45.) This demonstrates that a precursor to cresol is being diverted to form toluene and phenol. As discussed below this implicates a radical mechanism, especifically one involving methyl radicals.

It is of interest to know the relative reactivities of various compounds and the experiments in which anisole plus additive were reacted simultaneously provide a crude measure of this. Thus, the fraction of additive recovered can be compared with $(1)/(1_0)$ (Table IV). Although it is qualitatively observed that the additive reaction rates respond to Pr^{-1} changes in the same way as anisole or 2-butene,[4] insufficient data are available to establish a rate law. For this reason and others, the quantitative nature of the comparisons is of dubious value. The data are, however, quite interesting. They suggest that virtually all organic molecules will react under similar conditions, i.e., that plasmolysis is not very selective in an intermolecular competition. It also shows that trapping experiments will generally suffer from the fact that the trap is independently reactive. Only nonane can really be considered unreactive under these conditions.

The dynamics results are summarized as follows, the rate law for anisole is consistent with rate-limiting electron impact where the number and energy of the electrons controls the rate. It has also been shown that a number of organic compounds give similar overall rates and rate laws of the same form as that for anisole. It, therefore, seems that this will be a common kinetic situation. The primary kinetic effect of organic additives is to cool the plasma in the same way as does anisole. The results, are, therefore, self-consistent and indicate that those electrons in the plasma which cause reactions are indiscriminate. They are cooled almost equally by a variety of compounds and activate these compounds at similar rates. Finally, it is emphasized that there is a rather narrow range of Pr^{-1} values where useful plasma reactions can be performed.

Intermediates and Mechanisms. In this section the products and trapping experiments are interpreted in terms of mechanisms involving methyl radicals. Then isotopic labeling studies are presented. They are consistent with a major pathway involving dissociation and recombination via methyl radicals, but also demand a second pathway leading to the cresols.

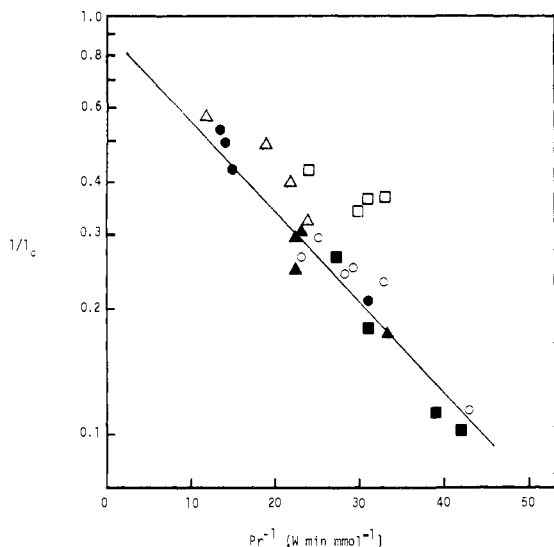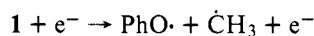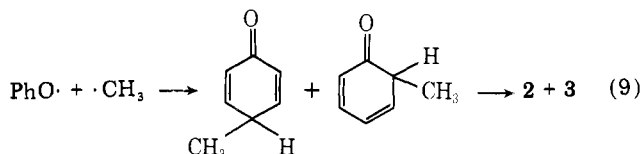It is found that ethane is a major product and this is sug-

Figure 5. Kinetics of anisole plasmolysis with organic additives: O, tripropylamine: ●, benzene; □, cumene; ■, benzonitrile; △, benzaldehyde: ▲, nonane.

Table IV. Relative Reactivity of Additives to Anisole

Additives	$\dfrac{\log\,[(Add)/(Add_0)]^a}{\log\,[(1)/(1_0)]}$
Nonane	0.11[b]
Benzonitrile	0.25
Tripropylamine	0.26[b]
Cumene	0.33
Benzene	0.30
Benzaldehyde	1.55

[a] Average of values except extremely deviating one, if any. Relative standard derivation of each value is ~10%, unless stated otherwise. [b] Relative standard deviation is ~30%.

and benzaldehyde have no effect on the rate of reaction, but produce larger amounts of phenol and toluene at the expense of cresol formation. This can be interpreted in terms of the above mechanism since methyl radical scavenging could lead to toluene and inhibit cresol formation. Although methyl will react directly with benzene, the results suggest that combination of phenyl and methyl radicals is an important scavenging route. Phenyl radicals are thought to be formed in both benzene and benzaldehyde plasmolysis[12,13] and, indeed, we find biphenyl as a product under these conditions.

$$PhH \rightarrow Ph\cdot \rightarrow Ph\text{--}Ph$$
$$\uparrow$$
$$PhCHO$$

$$Ph\cdot + CH_3\cdot \rightarrow PhCH_3$$

$$Ph\cdot + PhO\cdot \rightarrow PhOPh$$

In these trapping experiments, phenyl ether is also formed and this could be similarly interpreted in terms of combination of phenoxy and phenyl radicals. When $C_6H_5OCD_3$ is reacted in the presence of benzene (see below), the trapped product is $C_6H_5CD_3$.

The effect of other additives on the products is smaller and, therefore, difficult to interpret. Cumene and tripropylamine gave a higher phenol yield than that predicted in absence of additives, while nonane and benzonitrile displayed no substantial effect. Because cumene and tripropylamine can be involved in the free-radical chemistry by donating hydrogen atoms and by forming radicals by plasmolysis chemistry, their effect is not surprising. Nonane and benzonitrile are, on the other hand, relatively inert compared with anisole and it is not surprising that they have no effect.

In summary then the data strongly suggest a dissociation-recombination mechanism involving methyl radicals. Phenoxy radicals are consistent with the results, but the involvement of ions like phenoxonium and phenoxide cannot be ruled out. Because these plasmolyses take place in the presence of a high flux of electrons, interconversion of neutral and ionic intermediates is quite feasible. The problem of redox reactions can be formalized by a "scheme of squares", in which the species are interconnected by electron transfer or chemical steps. For anisole isomerization to p-cresol, see Scheme IV.

Some soft evidence against a pathway involving cation radical formation and fragmentation exists. Since tripropylamine is a good base and a good electron donor, its inability to trap or quench intermediates is suggestive that cations are not intermediates on the route to products. One would expect, for example, that tripropylamine (IP = 7.23 eV) would quench anisole (IP = 8.22 eV) cation radicals. This expectation is reinforced by measurement of the ion cyclotron double resonance spectrum of a mixture of anisole and tripropylamine which shows that this charge transfer is quite facile. The ICR and mass spectra of anisole also suggest that direct cleavage of anisole$^+\cdot$ to phenoxonium is not a favorable process since the m/e 93 peak has a very low intensity.

gestive of methyl radical intermediates. Therefore, one acceptable mechanism for the formation of phenol and ethane is an electron-impact-induced fragmentation to phenoxy and methyl radicals. In terms of free-radical thermodynamics this is the least endothermic (+61 kcal/mol) fragmentation and it is, therefore, a reasonable pathway.
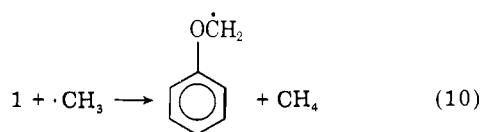
$$1 + e^- \rightarrow PhO\cdot + \dot{C}H_3 + e^-$$

$$PHO\cdot \rightarrow PhOH$$

$$CH_3\cdot \rightarrow C_2H_6$$

If these species are present then they are also expected to recombine to form the cresols (eq 9). This would accommodate

$$PhO\cdot + \cdot CH_3 \longrightarrow \text{(structures)} \longrightarrow 2 + 3 \quad (9)$$

the important experimental result of crossover between methylanisole and phenetol found by Suhr and Weiss. The formation of only ortho and para products, not meta, is expected via this route and the ortho/para ratio is about that expected. A study of phenoxy–methyl combination at 10 Torr and 500 K by Mulcahy and Williams,[10] showed that o,p-cresol are the major products. They found that ortho/para = 1.1. Because of the difference in reaction conditions, the quantitative difference in ortho/para between this and the plasmolysis ortho/para, 1.8, cannot be interpreted.

The virtual absence of methylanisole in the product mixture is not surprising because methyl radicals preferentially attack anisole on the methyl group[11] (eq 10). The fate of the new

$$1 + \cdot CH_3 \longrightarrow \text{(structure } O\dot{C}H_2) + CH_4 \quad (10)$$

radical, $PhOCH_2\cdot$, can only be speculated upon. The study cited above suggested that it would lead to $PhOCH_2CH_3$ and $PhCHO$. These are found as minor plasmolysis products.

In the presence of additives some trapping of intermediates is found. The most important of these results is that benzene
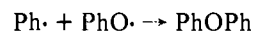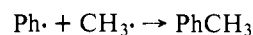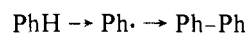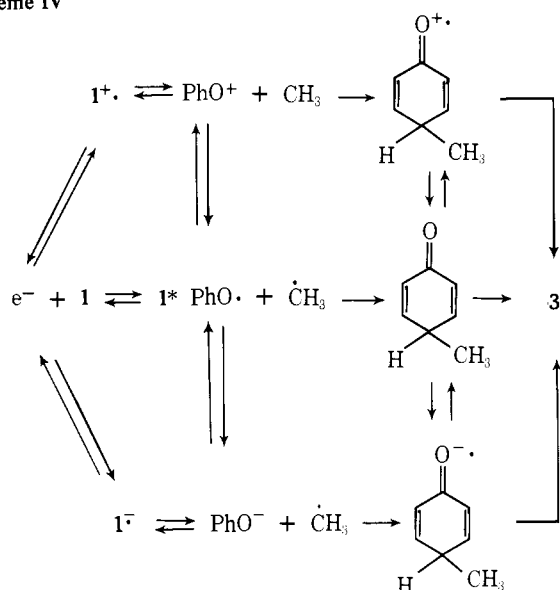
Scheme IV

Another interesting comparison experiment is anisole photolysis. Photolysis in alcoholic solvents gave a similar product distribution to that in our study.[14,15] There is one report on the gas-phase photolysis of anisole.[16] Each of these seems to indicate that formation of methyl and phenoxy radicals followed by recombination takes place. We reiterate, however, that comparison experiments are interesting but not definitive. If one wants to know the mechanism in an ionized gas it must be directly studied.

Experiments have also been carried out with four different deuterated anisole derivatives, $C_6H_5OCD_3$, *o*-anisole-d_1, *m*-anisole-d_1, and *p*-anisole-d. It is first noted that deuterium substitution had no effect on the rate of anisole reaction or the product yields. Thus, there are no observable kinetic isotope effects. The more interesting results are the deuterium contents of the products as revealed by gas chromatography–mass spectrometry. The data in Table V were obtained after a water wash which will convert any O–D material to O–H. In each of the four cases the recovered anisole had an unchanged deuterium content. In the cases of *o*-, *m*-, and *p*-anisole-d_1, the product phenol also had the same deuterium content as the initial anisole. Phenol from $C_6H_5OCD_3$ was undeuterated. This demonstrates that intramolecular scrambling processes are unimportant. This result is of particular interest because it has been shown that the cyclopentadiene products from C_6H_5OD plasmolysis have undergone intermolecular H,D exchange.[17] The present result for phenol is consistent with any dissociation–recombination mechanism including those cited above involving methyl radicals. We note further that, when $C_6H_5OCD_3$ was run in the presence of benzene, the cross-product, toluene, was trideuterated in agreement with the proposed scavenging mechanism. One final observation is that the mass spectrum of the phenol from *p*-anisole-d before water washing is almost purely d_1. This suggests that the phenolic hydrogen does not primarily arise from the para position.

The results obtained for the deuterium content of the cresols are more complex. The only simple case is that from *m*-anisole-d_1 where both **2** and **3** were found monodeuterated as expected. The cresol products from the other three deuterated compounds give results which are internally consistent and demand that there is another pathway in addition to simple methyl radical recombination.

Consider first the results from $C_6H_5OCD_3$. Both *o*- and *p*-cresol are found to be primarily trideuterated as expected, but there is also a d_2 component (5–10%). Because of scrambling processes in the mass spectrometer the exact amount and positions of the deuteriums are unclear.

Table V. Isotope Retentions in Plasmolysis Products[a]

Reactant	4, %	2, %	3, %
o-Anisole-d_1[b]	93	78	94
m-Anisole-d_1[b]	94	91	93
p-Anisole-d[b]	97	92	21
Methylanisole-d_3[c,d]	0	92	87

[a] Relative deuterium content based on that of the starting compounds. For absolute deuterium contents see Experimental Section. Recovered anisole was 99% unchanged in deuterium content. [b] Products were d_1 or d_0. [c] Products were d_3 or d_2. [d] Plasmolysis with benzene gave the same deuterium contents within experimental error. Toluene analyzed for 89% $C_6H_5CD_3$.

In the reaction of *p*-anisole-d, the *o*-cresol is clearly d_1. The *p*-cresol is, however, a mixture of d_0 ($\sim$80%) and d_1 ($\sim$20%) (eq 11). The position suggested for the deuterium is one which
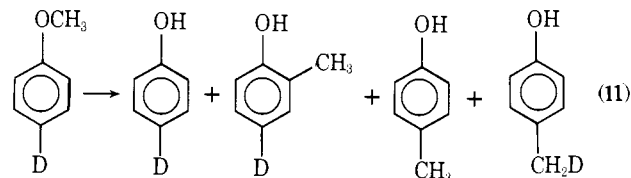
allows a self-consistent explanation. It cannot be ascertained by mass spectroscopy.

Analogous results arose from the plasmolysis of *o*-anisole-d_1 in that the *p*-cresol was monodeuterated but the *o*-cresol contained more deuterium ($\sim$75% d_1) than the statistically expected 50%. A similar positioning of the extra deuterium on the methyl is suggested; thus, a migration of deuterium from ortho to meta should have lead to a decreased deuterium content for the *o*-cresol obtained from *m*-anisole-d_1. Likewise the proper d_1 content of the *p*-cresol from *o*-anisole-d_1 indicates that *o*–*p* rearrangement is not involved. If the supposition that the minor reaction involves net insertion of a $CH_2(CD_2)$ into an *o*- or *p*-CH(CD) bond is correct, it suggests the involvement of carbene. Further speculation is unwarranted. It is simply noted that the major route appears to involve a methyl radical recombination and the minor ($\sim$20%), a net insertion of CH_2.

Experimental Section

Materials. Purity of anisole (Aldrich Co.) was checked by GC and found to be 99.5+%. The *o*-, *m*-, and *p*-anisole-d_1 were prepared by reaction of deuterium oxide and Grignard reagents of the corresponding bromoanisoles, which were found to be free of isomers. The methoxyanisole-d_3 was prepared by reaction of sodium phenoxide with methyl-d_3 iodide. All deuterated anisoles were purified up to 99+% by distillation. The extents of labeling were 82, 87, 72, and 98% for *o*-, *m*-, and *p*-anisole-d_1 and methoxyanisole-d_3, respectively. All other chemicals were obtained from commercial sources and similarly checked for purity prior to use.

Apparatus. The apparatus A is the same as described previously[4] except that the reaction chamber was located vertically in the present work. The apparatus B is shown schematically in Figure 1. The two reactors have similar dimensions, except that B is equipped with dual reactant reservoirs. An inductive coupling using an eight-turn coil from a $\frac{1}{8}$-in. o.d. copper tubing and a balancing circuit consisting of a variable capacitor led to the outlet of the rf generator (International Plasma Corp. Model PM 105D).

Procedure. Anisole and additives were separately taken into the flasks with Teflon needle valves and weighed after degassing by the freeze–pump–thaw method. The whole apparatus was evacuated. After traps were placed in dry ice–acetone and liquid nitrogen, the flow of reactants was started by partially opening needle valves. The flow rate (r) was controlled by the extent of valve opening and temperature of reservoir baths. The plasma was then generated by turning on the rf generator. The applied power (P) was measured and in every case the circuit was balanced so that the reflected power was negligible. After a specified period of time (usually 10–15 min), the power

was turned off, and the flow stopped. After the whole apparatus was isolated from the vacuum pump, dry air was introduced and the traps were warmed to room temperature. Finally, reactant reservoirs and traps were weighed to determine the amount of reactants passed and products collected in traps. Flow rate (r) was calculated from the amount of material lost from the reactant reservoir and the elapsed time during plasmolysis.

Analysis. Analysis of products collected in cold traps was carried out by means of GC. According to the additives, various stationary phases were used for liquid products as follows: silicone SE-30, Carbowax 20M, silicone OV-17, silicone QF-1, and Bentone 34 especially for separation of m- and p-cresols. In either case, the solid support was Chromosorb W-HP, and the percentage of stationary phase was 10%. For gaseous products, Porapak P was used. Identification of products was achieved by coinjection of authentic samples with products mixture, and was confirmed by gas chromatography–mass spectrometry. For the purpose of quantitation, the weight factors of every component in the product mixtures were determined relatively to anisole.

The isotope retention in plasmolysis products of deuterated anisole was determined by comparison of gas chromatographic data and mass spectra obtained from the products and unlabeled standard compounds. In the comparison, after correction for naturally occurring ^{13}C, the molecular ion (M) peak, M − 1 peak, and M − 2 peak were used. As the standard spectra of deuterated compounds were not available except for a few compounds,[18] following assumption was made for the hydrogen loss giving these peaks of interest. For anisole, the hydrogen loss takes place predominantly at methyl. On the other hand, for the other products, all hydrogens are equivalent. In both cases, the isotopic effect is not important. The assumption above was not critical for anisoles, phenols, and singly deuterated cresols. Furthermore, even for multiply deuterated cresols, it seems unlikely to cause considerable error in estimating the isotope retention.

References and Notes

(1) For a recent review, see "Techniques and Applications of Plasma Chemistry", J. R. Hollahan and A. T. Bell, Ed., Wiley, New York, N.Y., 1974; H. Suhr, *Angew. Chem., Int. Ed. Engl.*, **11**, 781 (1972).
(2) H. Suhr and R. I. Weiss, *Justus Liebigs Ann. Chem.*, **760**, 127 (1972).
(3) H. Suhr and R. I. Weiss, *Z. Naturforsch. B*, **25**, 41 (1970).
(4) J. G. Huntington and L. L. Miller, *J. Am. Chem. Soc.*, **98**, 8101 (1976).
(5) M. Tezuka, R. E. Drews, and L. L. Miller, unpublished work.
(6) A. T. Bell in ref 1, Chapter 1.
(7) The variation in rate with P and r could come from variations in electron distribution, electron energies, rates of interspecies energy transfer, residence time in the plasma region, or simply from the rate law for the specific reactions. Changes in product composition (ratios) could also arise from all of these factors. In addition, the possibility of converting primary products to other materials has often been suggested and a major change in mechanism with conditions is not unlikely.
(8) The above derivation leaves unclear the reasons why $k_1 f(\epsilon)$ is a linear function of P/p. One might suspect that knowing the number density of electrons (Ne^*) with energies greater than some limiting value for a quantized excitation and the average cross section for excitation by these electrons would be useful. Appropriate experimental data for reacting organic plasmas does not appear to be available.
(9) H. Suhr and G. Kruppa, *Z. Phys. Chem.*, **105**, 147 (1977).
(10) M. F. R. Mulcahy and D. J. Williams, *Nature*, **199**, 761 (1963); *Aust. J. Chem.*, **18**, 20 (1965).
(11) M. F. R. Mulcahy, B. G. Tucker, D. J. Williams, and J. R. Wilmshurst, *Chem. Commun.*, 609 (1965); *Aust. J. Chem.*, **20**, 1155 (1967).
(12) R. Weisbeck, *Chem. Ing. Tech.*, **43**, 721 (1971).
(13) H. Suhr and G. Kruppa, *Justus Liebigs. Ann. Chem.*, **744**, 1 (1971).
(14) J. J. Houser and M.-C. Chen, *Chem. Commun.*, 1447 (1970).
(15) J. J. Houser, M.-C. Chen, and S. S. Wang, *J. Org. Chem.*, **39**, 1387 (1974).
(16) F. Bayrakceyen, *Middle East Tech. Univ. J. Pure Appl. Sci.*, **9**, 51 (1976); *Chem. Abstr.*, **85**, 176543y (1976).
(17) A. Szabo, Thesis, University of Tubingen, Tubingen, West Germany, 1975, pp 142.
(18) Mass spectra of methylanisole-d_3 and methyltoluene-d_3 were reported by F. Meyer and A. C. Harrison, *Can. J. Chem.*, **42**, 2008 (1964), and H. M. Grubb and S. Meyerson, "Mass Spectrometry of Organic Ions", F. W. McLafferty, Ed., Academic Press, New York, N.Y., 1963, pp 491, respectively.

Synthesis of Parazoanthoxanthins and Pseudozoanthoxanthins

Manfred Braun, George Büchi,* and Dean F. Bushey[1]

Contribution from the Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139. Received September 6, 1977

Abstract: Parazoanthoxanthin A (**3**) and pseudozoanthoxanthin A (**4**), the least substituted zoanthoxanthins, a group of highly fluorescent marine natural products, have been synthesized by acid-catalyzed oxidative coupling of 2-amino-4(5)-(2-hydroxyethyl)imidazole (**7**), its dibenzoate **8**, 2-benzoylamino-4(5)-vinylimidazole (**16**), and 2-amino-4(5)-(1-hydroxyethyl)imidazole (**26**).

Among the multitude of new natural products isolated from marine organisms[2-5] the zoanthoxanthins[6-10] produced by colonial anthozoans, animals belonging to the order of Zoanthidae, occupy a special position. The highly fluorescent pigments were found to contain new aromatic ring systems and those known today belong to either the parazoanthoxanthin (1,3,5,7-tetrazacyclopent[*f*]azulene) or the pseudozoanthoxanthin (1,3,7,9-tetrazacyclopent[*e*]azulene) group. Within the two structural series the metabolites were shown to differ only in the number and position of *N*-methyl groups. Chemical transformations and spectral analyses of these pigments provided incomplete insight into their molecular structures and those of zoanthoxanthin (**1**)[6,7] and paragracine (**2**)[11,12] were established by x-ray analyses. The zoanthoxanthins can formally be considered to be dimers of a hypothetical C_5N_3 unit and the Italian investigators[9] were the first to suggest that the monomer used by nature might be arginine derived. To verify the chemical basis of this biogenetic hypothesis we have prepared parazoanthoxanthin A (**3**) and pseudozoanthoxanthin A (**4**) from the four monomers **7**, **8**, **16**, and **26**. Initial work[13] concentrated on the preparation and use of the primary alcohol **7**. Subsequent studies described in this paper included the secondary alcohol **15** and the vinylimidazole **16**.

Reduction of the commercially available lactone **5** with sodium amalgam in aqueous ethanol[14] yielded a diastereomeric mixture of hemiacetals **6**. The crude product was condensed with cyanamide[15] and the resulting intermediate cyclized and dehydrated to 2-amino-4(5)-hydroxyethylimidazole (**7**). The