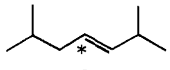
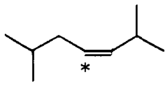
References and Notes

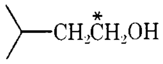
(1) For a recent review of this process, see G. Henrici-Olivé and S. Olivé, *Angew. Chem., Int. Ed. Engl.*, **15**, 136 (1976).
(2) J. M. Manriquez, D. R. McAlllster, R. D. Sanner, and J. E. Bercaw, *J. Am. Chem. Soc.*, **98**, 6733 (1976).
(3) M. G. Thomas, B. F. Beier, and E. L. Muetterties, *J. Am. Chem. Soc.*, **98**, 1296 (1976).
(4) Union Carbide, West German Patent 2262318 (1972).
(5) G. C. Demitras and E. L. Muetterties, *J. Am. Chem. Soc.*, **99**, 2796 (1977).
(6) L. I. Shoer, K. I. Gell, and J. Schwartz, *J. Organomet. Chem.*, in press.
(7) ^{13}C NMR for $(i\text{-}C_4H_9)_2Al\text{-}O\text{-}CH(CH_3)_2$, δ 67 (prepared from $(i\text{-}C_4H_9)_2AlH$ and acetone).
(8) T. J. Hurley, M. A. Robinson, J. A. Scruggs, and S. I. Trotz, *Inorg. Chem.*, **6**, 1310 (1967).
(9) Olefins **3** and **4** and 2-*m*ethyl-4-butanol are also obtained as by-products presumably by alkylation of CO, reduction, and, for **3** and **4**, elimination.



3



4



The assignment of structures for **3** and **4** is based on ^1H and ^{13}C NMR and mass spectral analysis. Using labeled ^{13}CO, it is observed that carbons marked (*) are specifically enhanced in ^{13}C. A small amount of 2-methyl-1-propanol is also observed. This alcohol is likely formed from adventitious oxygen in the workup procedure and contains no ^{13}C (above natural abundance) when ^{13}CO is used. Approximate amounts of **3** and **4** (combined) and 2-methyl-4-butanol, relative to CH_3OH (for Zr:Al::1:3), are 0.5 and 0.07, respectively.
(10) β-Hydride loss from DIBAH at 110 °C is well known. Under these much milder conditions it is possible that a Zr species acts to *abstract* this hydride. Such β-hydride abstraction from main group alkyls is well precedented (for example, see J. M. Jerkunica and T. G. Traylor, *J. Am. Chem. Soc.*, **93**, 6278 (1971)).
(11) G. E. Maciel, J. W. McIver, Jr., N. S. Ostlund, and J. A. Pople, *J. Am. Chem. Soc.*, **92**, 1 (1970).
(12) H. Pichler, H. Schulz, and M. Elstner, *Brennst. Chem.*, **48**, 78 (1967); M. A. Vannice, *J. Catal.* **37**, 449 (1975).
(13) This sequence parallels results obtained for the reduction of transition metal carbonyls by $NaBH_4$ (C. P. Casey and S. M. Neumann, *J. Am. Chem. Soc.*, **98**, 5395 (1976)).
(14) A scheme for reductive polymerization of CO in the Fischer–Tropsch process has been proposed.[1]

Larry I. Shoer, Jeffrey Schwartz*
Department of Chemistry, Princeton University
Princeton, New Jersey 08540

Received May 16, 1977

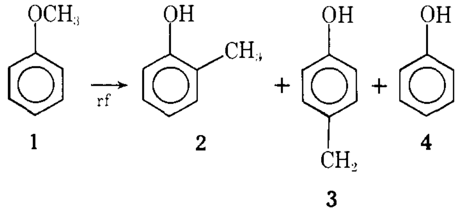
Kinetics of Anisole Plasmolysis

Sir:

Organic reactions induced by a glow discharge plasma have been used for purposes as diverse and exotic as modelling prebiotic synthesis, investigation of gas phase, organic ion chemistry, the preparation of thin polymer films, surface modification of solids, and organic synthesis.[1] Interpretation and application of the results of all of these studies are, however, hampered by the absence of a fundamental understanding of the dynamics and mechanisms in reactive, organic plasmas. We have sought to rectify this situation and have undertaken studies of the cool plasmas generated in a radio-frequency discharge. We demonstrate here the feasibility of applying kinetic methods and relate the observations to a theory in which the number and energy of the electrons in the plasma control the rate of reaction and, therefore, to a certain extent also the product ratios.

The apparatus is very similar to that previously described[2] except that dual reactant reservoirs were used. This allowed two compounds to be simultaneously flowed through the reactor with independently controlled flow rate. A bulb-to-bulb distillation at pressures from 0.02 to 0.2 Torr flows material through the discharge zone. A 13.6-MHz radio-frequency generator is inductively coupled to the system via a copper coil wound around the outside of the glass reaction tube and when power is applied a plasma, an ionized gas, is produced. After the material exits from the plasma it is collected in a liquid nitrogen trap and eventually analyzed by gas chromatography. The applied power (P) was measured and in every case the circuit was balanced so that the reflected power was negligible. Flow rate (r) was calculated from the amount of material lost from the reactant reservoir and the elapsed time during plasmolysis.

The plasmolysis of anisole (**1**) was chosen for study. Suhr and Weiss[3,4] had 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 alkylanilines were shown to react similarly. The isomerization to form *o,p*-cresol is a simple, yet unique, reaction and has been proposed to involve an intermolecular, ionic mechanism. Therefore, this was an especially interesting reaction for further study.



Anisole plasmolysis gave the products previously reported and some polymer. The extent of conversion of anisole (the rate) and the product ratio[5] depends on the applied power (P) and the flow rate (r). Qualitatively, low P and/or high r give low conversion and favor the formation of the cresols over phenol. This kind of observation has been previously reported for the reaction of 2-butene and arguments were put forward there to support the idea that the number and energy of the electrons in the plasma controlled both the rate and product ratio in that reaction.[2]

Quantitative interpretation of the anisole data depends upon 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 ($\sim 5 \times 10^{11}$ 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 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(ϵ).[6]

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

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

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 ($[\mathbf{1}]/[\mathbf{1}]_0$). Note that there are two parts to the right-hand side of this equation, an anisole plus electron rate and f(ϵ) 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 not known and may be complex. It is, however, clear that k should be some function of P/p.[6] We

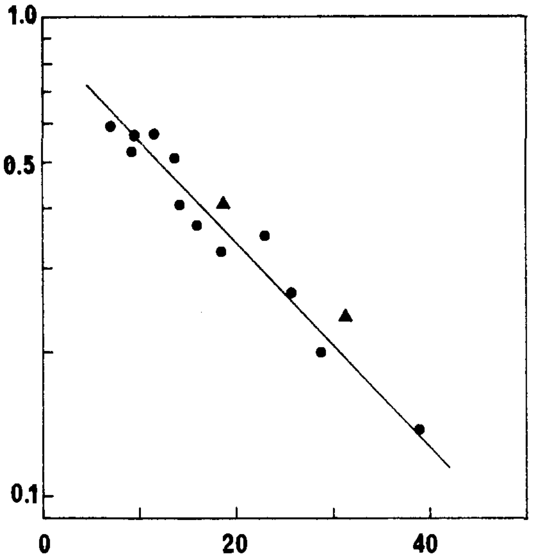


Figure 1. Kinetics of anisole plasmolysis: ●, anisole alone ▲, anisole plus argon (0.2 Torr). Ordinate, $[\mathbf{1}]/[\mathbf{1}]_0$; abscissa, P/r (W min/mmmol).

will assume that over the range of P,p studied there is a direct relationship. Therefore

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

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

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

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

Comparison of theory with experiment is shown in the semilog plot, Figure 1. The least-squares line is $-\log([\mathbf{1}]/[\mathbf{1}]_0) = 0.021(P/r) + 0.05$. 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. Above this r value, τ varies substantially. The linear correlation with intercept of zero demonstrates that $f(\epsilon)$ controls the rate of reaction.

Measuring the effect of additives on plasma reactions is a potentially useful mechanistic probe. One would, for example, like to divert or quench reaction intermediates or modify $f(\epsilon)$ with additives. Data for runs made with argon show that the added gas (0.2 Torr) is essentially inert. Thus, the rate and the product ratio $(\mathbf{2} + \mathbf{3})/\mathbf{4}$ are those found in the absence of argon. It is important to note that the gas is present in large excess so that the total pressure is relatively high. Similar behavior was previously noted for the 2-butene reaction. It is now interpreted to indicate that argon, at these pressures, is not significantly involved in determining the $f(\epsilon)$ of the organic reactions. This 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.

A variety of organic compounds have been used as additives to the anisole reaction. An initial survey demonstrated that these compounds had no effect when present in small amounts ($P_{\text{add}}{}^0/P_1{}^0 < 0.05$). Experiments in which the additive comprises a substantial portion of the mixture reveal kinetically interesting results. Data for tripropylamine, benzonitrile, and nonane are shown in Table I. In contrast to the noninvolvement of argon, these additives act to cool the plasma in the same way as anisole. Thus, Figure 2 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. The line shown in Figure 2 is the least-squares line from Figure 1. This result is fully consistent with the above discussion where the rate is determined by electron impact on anisole and $f(\epsilon)$ is determined by the total pressure of organic. It implies that $f(\epsilon)$ is not very sensitive to the structure of complex organic compounds.[8]

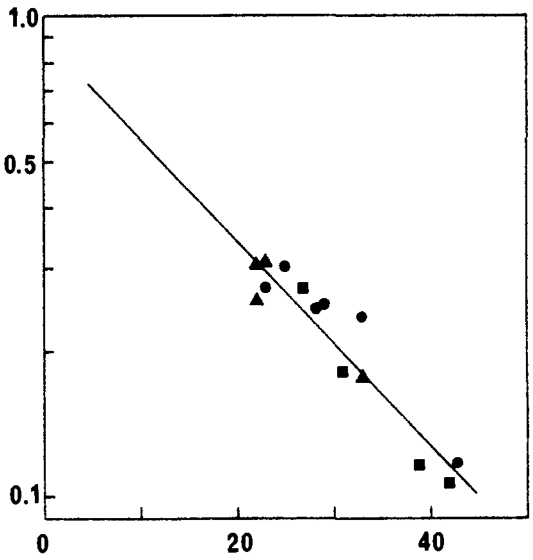


Figure 2. Kinetics of anisole plasmolysis with additives. ▲, with nonane; ●, with tripropylamine; ■, with benzonitrile. Ordinate, $[\mathbf{1}]/[\mathbf{1}]_0$; abscissa, P/r (W min/mmol).

Table I. Plasmolysis of Anisole with Additives[a]

r_1, mmol/min	r_{add}, mmol/min	$[\mathbf{1}]/[\mathbf{1}]_0$[b]	Recovd additive, %
	Nonane		
0.341	0.575	0.17	76.5
0.371	0.999	0.30	96.8
0.625	0.663	0.30	93.7
0.902	0.438	0.25	84.7
	Tripropylamine		
0.363	0.813	0.30	85.5
0.480	0.219	0.13	38.6
0.522	0.380	0.24	62.0
0.532	0.745	0.27	75.9
0.549	0.480	0.25	68.9
0.739	0.317	0.24	75.0
	Benzonitrile		
0.305	0.799	0.27	73.0
0.336	0.377	0.11	59.8
0.589	0.180	0.13	61.3
0.605	0.362	0.18	63.0

[a] All runs at $P = 30$ W. Product analyses to be reported. [b] Moles of anisole recovered/moles passed through the reactor.

There are a number of further aspects upon which this treatment impinges. There are, for example, correlations of reactivity between different compounds and correlations of product yield with P/r. These aspects will be elaborated on in a full paper. The eventual goal is obviously to use kinetics to help reveal the reaction mechanism. We believe that the kinetic observations and model constructed for anisole will prove to be quite general. Although the data are more limited, we have made similar observations on 2-butene plasmolysis[2] and several other compounds behave similarly. This approach should then lead to a better understanding of plasma chemistry and, hopefully, to useful applications.

Acknowledgment. This work was supported by the National Science Foundation.

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.

(2) J. G. Huntington and L. L. Miller, *J. Am. Chem. Soc.*, **98**, 8101 (1976).

(3) H. Suhr and R. I. Weiss, *Justus Liebigs Ann. Chem.*, **760**, 127 (1972).

(4) H. Suhr and R. I. Weiss, *Z. Naturforsch, Teil B*, **25**, 41 (1970).

(5) Product yields have been measured for every run and will be reported in a full paper.

(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) We predict that some dependence of f(ϵ) on structure will be revealed in more careful and extensive studies and may be present, but obscure, in the present data. Surely, all organics are not exactly the same!

Meguru Tezuka, Larry L. Miller*

Department of Chemistry, University of Minnesota

Minneapolis, Minnesota 55455

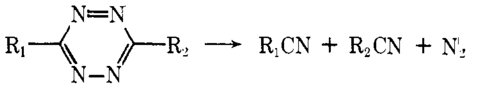
Received April 25, 1977

Measurements of the Relative Chemical Reactivity of Triplet Spin Substates

Sir:

In this communication we report the first direct measurement of relative *chemical reactivity* for separate spin components of a triplet state. The three spin substates, T_x, T_y, and T_z of a triplet state contain differing amounts of singlet character due to the anisotropy in the spin-orbit coupling. In the event that the chemical reactions of the molecule in its triplet state depend on this singlet character, we expect that the reactivity will differ for the three spin substates. One obvious example where such differences might be expected is when the primary step in the reaction involves an intersystem crossing from the triplet state into a highly vibrationally excited singlet ground state, as appears to be one mechanism for some simple molecular predissociations.[1] Recently Leung and El Sayed[2] have made the first measurements on the *photochemistry* of a triplet state, elegantly showing by microwave techniques how different sublevels of T_1 are photochemically degraded at different rates in $T_1 \rightarrow T_n$ transitions.

In previous work[3-6] we have shown that singlet and triplet excited states of *s*-tetrazine and its derivatives, dimethyl- and phenyl-*s*-tetrazine, undergo an efficient dissociation of the type



Although the dissociation of the triplet state is four to five orders of magnitude slower than the singlet reaction, it is still at least two orders of magnitude faster than the radiative rate calculated from the singlet-triplet absorption strength.[3] For the present study we have used dimethyl-*s*-tetrazine for which the conventional phosphorescence decay time of 83 μs is presumed to measure the rate of the photochemical reaction[7] averaged somehow over the spin substates.

The principle of our experiment is to utilize a combination of low temperature (4.2 K) and relatively high magnetic field (55 kG) to maintain a system of oriented molecules in essentially one spin substate after direct excitation of the lowest triplet with a tunable dye laser. Measurement of the lifetime for radiative decay in the presence of the field then yields the decay for a particular substate. By choosing three mutually perpendicular field orientations, results can be obtained for three orthogonal spin substates. A single crystal of dimethyl-*s*-tetrazine was situated in the field of a superconducting magnet, directly immersed in liquid helium, and irradiated by a nitrogen pumped dye laser at 648 nm. The phosphorescence spectrum originated from a single site with 0–0 band at 13 053 cm^{-1}. The dye laser operated at 50 Hz and signals from ~20 000 pulses were averaged to obtain the lifetimes shown in Table I.

Table I

Magnetic field orientation[a] ($\lvert B{\cdot}x \rvert^2 = \mu_x^2$)	Lifetime (μs) of phosphorescence[b]
0.65	78.6 ± 0.4
0.32	107.1 ± 1.2
0.03	125.2 ± 1.4
Zero field (4.2 k)	83.2 ± 0.4

[a] Least-squares fit to an exponential over two and one half decades.
[b] From optical density measurements on the crystal.

For any orientation of the magnetic field, specified by μ, the decay constant of the triplet state resulting from a measurement of the total emitted light, is

$$k_\mu = Z^{-1} \sum_{m_s} k_\mu^{(m_s)} e^{-g\beta B_0 m_s/kT} \qquad (1)$$

where $g \simeq 2$, β is the Bohr magneton, B_0 the applied field strength, Z is the partition function for the spin sublevels, and $m_s = 0$ and ± 1. $k_\mu^{(m_s)}$ is the total decay constant for sublevel m_s at field orientation μ. For $B_0 = 55$ kG, $2\beta B_0/hc = 5.13$ cm^{-1}, whereas $kT/hc = 2.92$ cm^{-1}; thus it is a reasonable first approximation to take $Z \simeq 1$ and consider only the $m_s = -1$ sublevel. In eq 1 we have assumed rapid achievement of a Boltzman distribution amongst the spin sublevels, consistent with our observation of exponential decays for all field orientations. The decay of the light signal is therefore a measure of $k_\mu^{(-1)}$. The three orthogonal directions (μ) for the magnetic field in the table are referred to the out-of-plane (x) molecular axis. The $^1B_{3u} \leftarrow {}^1A_g$ transition of the tetrazine is known to be out of plane polarized;[4,5,8] so the trichroism of the single crystals provides the approximate absolute value of the cosines of the angles between the three principal absorption axes of the needle-like crystals and the x axis of the molecules. The magnetic field was directed along each of these three axes. The results of our measurements are shown in the table.

The T_x, T_y, and T_z content of the $m_s = -1$ sublevel depends on μ; the probability of measuring T_ζ (ζ = molecular axis; x, y, or z) in $m_s = -1$ is zero when μ is parallel to ζ, and 0.5 when μ is perpendicular to ζ. It is apparent from the data shown in Table I that the longest lifetime occurs when B_0 is nearly perpendicular to x and the shortest lifetime occurs when B_0 is closest to x. This result implies that the T_x substate undergoes chemistry[7] substantially more slowly than either T_y or T_z. In the case that the triplet state decay occurs into pure singlet vibronic levels, the specific rate for a particular $m_s = -1$ sublevel is given by

$$k_\mu^{(-1)} = \tfrac{1}{2}[(1 - \mu_x^2)k_x + (1 - \mu_y^2)k_y + (1 - \mu_z^2)k_z] \qquad (2)$$

also

$$3k = \sum_\zeta k_\zeta = \sum_\mu k_\mu^{(m_s)} \qquad (3)$$

where k is the decay constant at zero field with equilibrated spin substates, and μ_ζ is the cosine of the angle between the field and the ζ axis. Our measurements yield 1.2×10^4 s^{-1} for the decay at zero field and 1.0×10^4 s^{-1} for $3\Sigma_\mu k_\mu^{(-1)}$, neglecting the population of the $m_s = 0$ sublevel. This discrepancy is