RADIATION INDUCED EFFECTS IN ORGANIC SYSTEMS

PROGRESS REPORT

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GENERAL

This year has seen progress in two areas of interest: the nature of the decay kinetics in systems yielding geminate radical pairs upon irradiation and OH reactions with aromatic hydrocarbons. A paper on radical pairs in hydrated amino acids has appeared in print. Reprints are attached.¹

The work on geminate pairs has focused on the p,p' azoxy phenetole molecule, studied at low temperatures using both polycrystalline and single crystal systems. The results obtained appear to be somewhat different from those for the p,p' azoxy anisole system reported on earlier.² Preliminary results on both microwave power saturation studies and decay kinetics suggest that the species stable only at low temperatures is not behaving as one would expect of geminate pairs.

The gas-phase OH reactions have received considerable attention this year and a number of observations of interest have been made. Experimental results which are reliable have been difficult to obtain because of the usual problems associated with wall effects, exacerbated by the reactivity H_2O_2 in such systems. The experimental procedures have now been modified to produce reproducible results which can be interpreted as occurring in the bulk rather than as surface-modified. The most surprising result has been the observation of relatively large amounts of biphenyl produced from benzene by OH radical attack. This product has not been hitherto reported and may be of significance in connection with the growing concentrations of substituted biphenyls in the environment.

Further efforts to interpret the time sequence of events in the STCA experiment were made. It is clear that further experimentation involving adjustable time constants are necessary. Due to the personnel shortage mentioned below no experimental work was accomplished on this phase of the project. Efforts to secure a suitable person to follow up this work continues.

As mentioned, staffing has been a problem. At the present time the project is staffed by two full time, and one part-time technicians in addition to the principal investigator. Again this lowered level of activity has resulted in a small excess of funds. It is hoped that there funds can be carried over to the next contract period.

The principal investigator attended the two major conferences on radiation chemistry this past year: the Gordon Conference and the Radiation Research Society. He also continued his responsibilities with the Radiation Chemistry Data Center, although this term has now ended.

Capital equipment purchased on the contract since December 1979 includes UTI channeltron electron multiplier at a cost of \$1800.

SPECIFIC AREAS IN WHICH RESEARCH HAS BEEN PERFORMED

1. RADICAL REACTIONS IN AZOXY BENZENES AT LOW TEMPERATURES.

An extensive series of studies has been made of the radical recombination reactions in irradiated azoxybenzenes³. The most recent of these involved a low temperature (77 K) study of the radicals produced in p,p' azoxyanisole (PAA), where it was found that two radical populations existed. Stable only at lower temperatures was the geminate pairs formed by the removal of N_2O from a single molecule. These species account for about 70% of the total radical concentration. The remaining 30% consists of isolated radicals which are intact azoxy molecules with the radical site most frequently located on the aromatic nucleus. The existence of the geminate pairs was established by an analysis of the esr spectrum at half-field ($g=4$) and the power saturation behavior. These radicals were found to decay rapidly above 180 K, but not by a clean pseudo-first order process as one might expect for pair-wise decay. The radicals stable above 298 K decayed by a mechanism previously discussed.⁴

The data so-far collected on the p,p' azoxyphenetole (PAP) system are not in complete conformity with the observations noted above. Again, two radical species are observed at 77 K and only one is stable at room temperature and the former is a multiline spectrum while the room temperature radical produces a broad singlet. However no signal was detected at half field ($g=4$) and the power saturation be-

havior was not consistent with the presence of a large concentration of radical pairs. (see figures 1 and 2) An examination of figure 3 shows the same kind of stepwise decay occurring for the low-temperature radicals as was previously observed for the radicals stable at room temperature. This is inconsistent with the hypothesis that these radicals are geminate pairs decaying by recombination.

It is of further interest to note that with one exception the rate of radical loss with increasing temperature is reasonably linear. This can be seen from figure 3. The exception is in the temperature region in the vicinity of 136 K. Here decay of a much larger fraction occurs over a forty minute period than at lower temperatures where the stepwise character is much more pronounced. In the Waite theory stepwise decay results from a two-step process which has an appreciable activation energy for both processes: diffusive and recombination, with the former being rate determining. A stepwise behavior involving geminate pairs suggests, by analogy, an appreciable activation energy for reorientation followed by a rapid recombination process. Why this should be more pronounced for PAP than PAA remains to be discovered.

2. OH RADICAL REACTIONS

Considerable progress has been made in this area with the availability of the new equipment described in last

years report. Studies have been conducted involving, first of all, product identification; which has been largely ignored in previous studies in this field. Two major products have been identified: phenol and somewhat surprisingly, biphenyl. The formation of these products in a typical experiment is shown in figure 4. In this experiment the reaction chamber contained 1.0 torr hydrogen peroxide, 1.45 torr benzene and 32 torr argon in a total volume of 500 cc. The reaction chamber was maintained at a temperature of 25°C. It can be seen that at the end of 30 minutes illumination, using a single low pressure Hg lamp approximately 28 mtorr of phenol and 10 mtorr biphenyl have been produced. The apparent net formation of biphenyl quickly decreases and after about 20 minutes essentially ceases. This observation can be explained by reference to the fact that at 25°C the equilibrium vapor pressure of biphenyl is approximately 10 mtorr: thus biphenyl concentration in the gas reaches an equilibrium at this pressure.

Extrapolation of the linear portion of the curves yields a final ratio of phenol and biphenyl of about 2:1. This suggests that a common intermediate is involved in the production of the two substances.

That the rate of phenol formation is dependent upon OH-radical concentration is illustrated by an experiment in which the intensity of the light used to decompose the H_2O_2 was varied. The light intensity was varied in the ratio 1:2:4. The yield of phenol was found to be in

the ratio 0.65:1.2:2.2 for a fixed time of illumination in the linear portion of the production curves. While these ratios are not exactly equivalent they are close enough to suggest that the rate is controlled by the rate of H_2O_2 decomposition.

The effect of variation of initial H_2O_2 concentration has also been investigated. For a doubling in the H_2O_2 concentration an increase in the rate of formation by a factor of 1.5 was observed. This is similar to the consequence of increasing light intensity.

One experiment has been conducted at a higher temperature (91°C). The rate (in the linear region) was increased by a factor of 1.6. This increase may be the result of the usual activation factor or it may merely reflect changes in vapor pressure, leak rate or other parameters associated with the analytical procedure. This is being investigated further.

These observations coupled with the evidence found in the work of Davis, et al.⁵ suggest that the following mechanism may be responsible for the formation of phenol and biphenyl:

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Reprints Removed

can Range $\times 200$ G Time Constant 0.3 sec Modulation Amplitude $\times 1.0$ G Receiver Gain 2×10^3 Microwave Power 0.5 mW
 Field Set 3240 G Scan Time hrs 8 min Modulation Frequency $100k$ Hz Temperature $Varied$ $^{\circ}C$ Microwave Frequency ~ 9.1 GHz

Operator

Date $11/24/80$

Radical pairs gone at about $-103^{\circ}C$

Variable Temp. Dewar in place

RECORDED

GRAPHIC COPY

FILE

X-band Power Saturation of PAP crystals irradiated
and measured at 77 K. Signal Area (Arbitrary Units)
vs. $(\text{Power, mW})^{1/2}$.

LOCALIZATION OF THE STRENGTH

1

1.452 ton of BENZENE

32.2 ton total in Rx chamber

PRESSURE
PHENOL IN
REACTION
CHAMBER

RUN

#2 12/9/80

• # 12/9/50

26.1 ml of

22.1 mTorr

18.1 mTorr

14 m to R

RUN

+ 11.3 meter

● 廿

9.7 mtorr

○ 4

1. 8.0 m top

+ 6.4 mTorr

$$M_{\text{H}_2} = 94$$
$$r_{\text{e}}/e = 94$$
 $m/e = 154$
$$m/e = 154$$

time