

PRNC116

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PUERTO RICO NUCLEAR CENTER

MATRIX ISOLATION STUDIES OF THE GAMMA-RADIOLYSIS
OF HETEROCYCLIC MOLECULES

Technical Progress Report #3

A. Grimison and G. A. Simpson

April 1968

OPERATED BY UNIVERSITY OF PUERTO RICO UNDER CONTRACT
NO. AT (40-1)-1833 FOR U. S. ATOMIC ENERGY COMMISSION

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(CHEMISTRY (T1D-4500))

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Personnel. Participating:

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The results achieved in this project from May 1956 to April 1957

were previously presented in Technical Progress Reports No. 1 (PRIC

Publication No, 88) and 2 (FRNC Publication No, 99). The present Technical Progress Report reviews the results obtained in the period from April 1967 to April 1968, the time of preparing this report. As done before, it is convenient to divide the work into two sections, Experimental and Theoretical.

I, Absorption Spectra of Radical Intermediates at 77°K.

The general approach and techniques in this section of the work have remained the same as described in PRIC Publications No. 88 and 99. However, a series of absorption studies of intermediates produced in 2-methylpentane (5MP) have been initiated to parallel the emission studies reported in Part II of the Experimental Section (Table 1).

A specific attempt has been made to observe the radical anions of pyridine, pyrazine, pyridazine, and pyrimidine by radiolysis in 2-methyltetrahydrofuran (MTHF) as follows:

8. This stems from our earlier observation (see 99) of a high efficiency of electron scavenging for these azines and diazines. The spectra of species assigned to these radical anions have previously been reported by Hush et. al. (10) in their work the neutral heterocyclic molecules were reduced by metallic sodium in MIP at room temperature, The results from our radiolysis experiments are compared

with those of Hush in Table 2. The general agreement is very good, suggesting that the radical anions are among the species formed on gamma-radiolysis. This appears to be the first case where the importance of ionic intermediates in the radiolysis of heterocyclic compounds has been established,

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Considering the detailed comparison of the results for pyridine and the diazines, the agreement for pyridazine is excellent. The absorption at 354 nm in irradiated pyridazine in MTHF is observed to increase on bleaching the trapped electron band. This confirms the assignment of the 354 nm band to the pyridazine radical anion. For pyridine and pyrazine the slight variations observed from Hush's values have prompted us to undertake a detailed examination of these systems. Figure 1 shows the dependence of the absorption at 350 nm and 1200 nm in the irradiated pyridine-MTHF system of the initial pyridine concentration. The 1200 nm band corresponds to the position of the trapped electron band in MTF. The figure clearly shows how the trapped electron absorption decreases with increasing pyridine concentration. Simultaneously the 350 nm absorption decreases, however, this is mainly accounted for by residual absorption of the 1200 nm band into the 350 nm region. This residual absorption also decreasing with the trapped electron concentration, it is observed

that the 1200 nm band can never be completely scavenged by pyridine. A possible interpretation of this fact is that the anion has a band at 1200 nm, in addition to the 350 nm band. Two independent observations support this view. The first is obtained from experiments with photolysis (bleaching) into the 1200 nm band of gamma-irradiated pyridine-MTHF solutions. Since the 1200 nm band is mainly attributed to the trapped electron band in MTHF, photolysis in this band is expected to liberate electrons which can be captured by normal pyridine molecules, producing an increase in the concentration of the pyridine radical anion, and thus an increase in the 350 nm absorption. This is indeed observed in the concentration range below 4×10^3 M pyridine. However, at higher concentrations, bleaching,

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causes a decrease in the 350 nm absorption. This is compatible with an actual photolysis of the radical anion, occurring via its 1200 nm absorption, when this is appreciable relative to the trapped electron 1200 nm absorption. The second supporting observation stems from radiolysis experiments on pyridine in ^{34}P . In 3MP the trapped electron band occurs at 1600 nm, and in addition to this, bands at 360 nm and 1200 nm can be observed. Finally, the preliminary results of Pariser-Parr-Pople calculation for the pyridine anion reported later (Table 8) give the lowest energy transitions at 4.0 eV and 0.8 eV, in excellent agreement with the above assignment of 3.6 eV (550 nm) and 1 eV (1200 nm). The investigation of this system is continuing, and additional experiments have shown that the

Presence of water in the pyridine-MTig system completely suppresses the formation of the 350 nm band.

The work on solutes in the glassy Freon matrix (Fi) has continued, The preliminary note describing the characteristics of the matrix was Report (FRNC 99). At the suggestion of

appended to the previous Proceedings of the editors and reviewers of the Journal of Physical Chemistry, this note was extended to a full paper by the inclusion of our results on a number of heterocyclic molecules in MT, and is in press. A copy is appended to this report. The highlights include the characterization of cationic species formed by gamma-radiolysis of the FA matrix, The suitability of this matrix for stabilization of cationic intermediates is demonstrated by the detection of cationic species formed from several heterocyclic additives. In particular, the thiophene radical cation was

pyrrole radical cation. λ_{max} at 800 and 310 (nm), and the pyridine

radical cation λ_{max} at 380 nm.

in excellent accord with the Pariser-Parr-Pople calculations reported later

The results for pyrrole and pyridine are

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(Tables 8 and 9). These give pyrrole radical cation transitions at 1.2 and 3.8 eV as against the above assignment of 1.5 eV (800 nm) and possibly 4.2 eV (510 nm). The pyridine radical cation is calculated to have a transition at 3.2 eV, to be compared with the above assignment of 3.3 eV (380 nm),

The results obtained on gamma-radiolysis of indole in At (Table 2) are surprising in comparison with the photochemical results (A, Part IV), and also the flash photolysis studies of Grosveiner. The spectra suggest that if the 420 nm band reported in photolyzed indole is present, it may have been shifted by overlapping with the FM 585 nm band. Closely spaced maxima are observed in the region from 450 to 700 nm, and a strong band at 1100 nm. The latter band may be associated with the 420 nm band, assigned to the indole radical cation, which is likely product of the FM radiolysis.

However, the 1100 nm band could not be detected in the steady state or flash photolysis experiments. The complex maxima in the 450 to 700 nm region suggest the presence of at least one other species. Optical bleaching experiments and JAP radiolysis are being made on indole to clarify these

points,

II, Luminescence of Irradiated Glassy Solutions at 77°K

The purpose of the luminescence experiments is two-fold. The first is to determine whether gamma-irradiation produces species having different emission spectra when excited by ultraviolet light of a suitable wavelength.

The second is to search for recombination luminescence by infrared or thermal

excitation of the system subsequent to gamma-irradiation, A radiation

---Page Break---

a

ed luminescence has been observed in irradiated 3 we? and is considered a

to result from excitation of a charge separated state of the aliphatic

hydrocarbon, aii" has reported recombination luminescence of & 285°

number of aromatic solutes in JNP, stimulated by either infrared or thermal

excitation of the matrix, He attributes this luminescence to the result

of either electron-cation or cation-anion recombination. In the matrix,

depending upon solvent viscosity.

Luminescence studies have been limited almost exclusively to 2P

after a test on the ability of MKD to undergo thermally stimulated luminescence

in either MEP or Pi irradiated matrices, Hanill raintaine (private

communication) that the absence of an effect may be expected in MTHF since only anion additives are stabilized, A recombination event between that anion and a solvent cation would result in the excitation and decomposition of the solvent, In Pi the 1MPD is observed to form a colored, salt-like product on warming. Possibly recombination in this matrix involves bond scission between the cationic additive and a halide ion,

The results of the investigations into these effects are reported in Table 3 and Fig. 2. The luminescence spectra were obtained with an Aminco Soman Spectrophotofluorimeter using either the Aminco low temperature optical dewar for small 1/8" od silica tubes, or a square quartz dewar for larger 1 x 2 cm square optical cells, the larger cells provide greater intensity of luminescence than the smaller tubes,

although their use presents

some problems in detection of new emission bands, The square quartz dewar

itself emits a number of bands on excitation with
laser at 300, 400 and 555 nm,

Laser near 250 nm with

Thus, this dewar is used only for determining

emission bands resulting from thermal excitation, Infrared stimulation

has not been attempted so far,

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Figure 2 provides a demonstration of the thermal excitation experiment which is similar in principle to experiments which determine "glow

curves". The cell in the dewar is allowed to warm up by removing the

Liquid nitrogen from the dewar and monitoring the emissions by repeatedly scanning with the spectrometer. Thus, the time dependence of the emission spectra is obtained. The results for the luminescence of pure xP are

in good agreement with those of the Funsbashi group. Immediately after warming, luminescence near 425 nm is produced, At higher temperatures

this shifts to shorter wavelengths, due to an emission resulting from radiation-induced olefin production. When other compounds are dissolved

in MP, the IMP emission band is reduced in intensity and emission bands associated with the additive are produced. These effects have been observed for the following compounds: biphenyl, DNA, pyridine, Fyrazine, pyrrole, naphthalene (MIHF solvent), thiophene, toluene, and triphenylamine. The results with biphenyl and triphenylamine have been reported earlier by

Hasil and Skelly." Emissions from γ -irradiated toluene on warming have been observed previously by Brocklehurst et. al.,^o and from photolyzed toluene on uvvs excitation by Porter. The similarity of the thermoluminescence emission bands of toluene following γ -irradiation to those induced by u.v. excitation suggest that excitation of neutral benzyl radicals is also being produced in the thermoluminescence study.

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Seow FemuLta witch wore obatnad with Lrrwitated silica tubes

#1) are of eonniderate Intereats An absorption band with daar

AE 256 nm La produced on irradiation, and this band disappears on warming

Irradiation into this band was observed to produce an emission at 310 nm.

These effects are attributed to hydroxyl radicals arising from water sorbed on the surface of the silica for a number of reasons, Water is strongly

absorbed on silica

It is known that hydrogen atoms are produced by
radiolysis of this water, with an enhanced yield in the presence of hydroxyl
radicals. This is therefore indicated, although they have not been previously

Identified in this system, hydroxyl radicals are known to absorb in the
250 nm region of the spectrum, and have λ_{max} at 260 nm in aqueous solutions,
The hydroxyl radical exhibits an emission band at 306 nm in the glass phase?

A warm-up glow from irradiated solutions of pyridine in 34P
occurring at 350 nm has been observed, persisting for long times (10 to 20
minutes) after removal of the liquid nitrogen. The absorption spectrum has for
this solution λ_{max} at 360 and 1200 nm. The 1200 nm band has been assigned
to the pyridine anion (earlier), together with a band at 350 nm. The
cation shows a λ_{max} at 300 nm (attached preprint). The spectrum in MP
might therefore be due to the superposition of the radical anion and
radical cation spectra, the bands at 350 and 300 nm not being resolved.
The long-lived luminescence observed can therefore be tentatively assigned
to the recombination of cations and anions. This is expected to be a
diffusion-controlled reaction, but the low rate is compatible with the
high viscosity of the glass at these low temperatures, even after some

softening has occurred,

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A test can be made by a comparison of the temperature dependence of the absorption spectra and that of the emission spectra. A slight raise in temperature would be expected to liberate some of the trapped electrons to recombine with neutral pyridine molecules and pyridine cations to yield a low temperature luminescence, and a shift in the absorption maximum from 360 to 350 nm. At higher temperatures, the decrease in the absorption bands and in the long-lived luminescence should follow the

same kinetic

The phosphorescence from the triplet state of pyridine has been reported at 370 nm, this difference in wavelength is somewhat outside

the limit of experimental error. Nevertheless as a preliminary hypothesis the emitting species can be taken as the triplet state of pyridine until,

an exact comparison of the pyridine phosphorescence and the thermoluminescence

can be made,

TIL, Electron Spin Resonance of Redicytic Intemediates at 77°K

?The principal work on electron spin resonance has been related to Antemediates in the irradiated freon mixture (FM). Figure 3 shows some of the ESR spectra of irradiated FM obtained on a Varian E-3 ESR spectrometer at the Chemistry Department, University of Puerto Rico, The resonance associated with the degassed, irradiated sample and tube is very complex extending over 500 gauss (spectrum 3s), and containing unresolved structure. ?The analysis is further complicated by the hydrogen atoms and other resonances, which undergo changes on exposure to visible light, This suggests, ?that, in addition to hydrogen atoms and the hydroxyl radicals proposed in this report, another species absorbing in the visible region, such as the trapped electron or absorbed Hg^{0} may be present. (See Figure 3 b)

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Due to these factors, attempts were made to irradiate and take the ESR spectra of frozen FM droplets in liquid nitrogen. Unlike the absorption spectra, the ESR spectra are found to be strongly influenced by the presence of oxygen. Spectrum 3o was obtained by dropping aerated FA into liquid nitrogen, and spectrum 3a by extruding glassy, degassed Ai into liquid nitrogen, The lack of detailed structure in 3a compared to 3o indicates that some air contamination of FU has occurred despite precautions.

Bleaching experiments indicated that the principal effect of the ESR spectrum of photolyzing irradiated Mi with visible light (see attached Preprint for effects on the absorption spectrum) is to increase the

Fesonances in the center portion of the spectrm, near $g = 2$. This can be correlated with the increase in the absorption of irradiated M_i at wavee lengths ess then 300 nm on bleaching. The only ESR signals which decrease on bleaching are the extrene left to the spectrum (field approx, 2800 gause and frequency 9.2 gigacycles/sec), These signals can therefore be correlated with the positively charged species in irradiated PM with absorptions bands near 350 and 585 m, which are removed ty bleaching.

IV. Photochentstry of Arnatic Amines and Heterocyclic Compounds at 77°K

Recent evidence has denonstrated the generality of the biphotonic

Jonization of a large class of compounds,© via their triplet states, It is conceivable that radical cations of heterocyclic coupounds can be generated in this fashion, Since neutral radicals can also be produced via simple excitation transfer, photolysis provides an independent method of establish ing the nature of radiation induced intemediates.

Fhotolysis were carried out in 1 on square quartz cells in a square

optical devar with liquid nitrogen by exposing the devar to the full are

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of @ Muneralight R-51 low pressure mereury lamp, or an Osram H20 500 high

Pressure mercury lamp, In onder to test a theory of itanti1!? on the effect

of solvation in a polar solvent, and the effect of trapping a photoejected electron by a halogenated compound, all photolysis were repeated in Freon mixture (Fu), 2-methyltetrahydrofuran (MIP) and 3-methylpentane (34P). Measurements of spectra of photolyzed, degassed samples at 77°K were made in a Bausch and Lomb 505 Recording Spectrophotometer, Table I shows the results obtained for photolysis of aromatic amines in comparison with previous work. Three points arise from this table. The first is that the intensities employed are sufficiently high to produce appreciable photoionization. The results are in excellent accord with those of earlier workers, except for the failure to produce photoionization of diphenylamine. The results for diethyl-aniline and ethylaniline obtained here are the first reports of steady state, as opposed to flash photolysis, photolysis of these compounds. The hypothesis of Hanzi² is borne out by the results, since there is an enhancement of color formation in general in MTEF compared to MP.

A large number of heterocyclic compounds were first screened visually for photolysis, and then the absorption spectra determined in favorable cases. The results are summarized in Tables 5 and 6. Of the compounds screened in this manner, only one previously reported to photolyze gave negative results. Douzoul² et al. report a photoinduced absorption band of purine in aqueous solutions between 300 and 350 nm, together with ESR evidence for the solvated electron. The failure to observe similar results here is due to the fact that only visual observations were made.

The result with indole may be compared with the experiment of Grossweiner[®] in which indole was flash-photolyzed to yield the solvated

nL

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electron and band near 450 nm. However, in an earlier report[?] by the same author there was evidence for several bands in the range 400 to 600 nm in addition to the band near 500, which was assigned to a neutral radical at that time rather than the indole radical cation. The λ_{max} observed here is 439 nm at 120 ns. The difference may be due to solvent shifts, although there appears to be a discrepancy between the two Grossweiner papers, since the earlier paper reports the indole band at 439 nm. This is one case where a direct comparison with the radiolysis work is being made (Part I).

The absorption band produced at 370-400 nm on photolysis of Freon 11452 can be compared with the species produced by Hanil¹ and Bertin[®] by irradiation of methyl bromide or sec. butyl bromide in MP, and having λ_{max} at 360 nm. A band having a similar bleaching response has also been observed in the γ -irradiation of alkyl iodides in 3MP.²⁶ These bands have been assigned to the charge-transfer complex X.RK, arising from recombination of x_7 and R_t . The photolyzed Freon 11NR2 gives a bromine like color on warming, but the spectrum does not correspond to atomic bromine.

By analogy with Hanill's work, this absorption may arise from a charge transfer complex between Br and FM or FLLAB2.

The fact that only 15 out of the 50 compounds tested gave colored intermediates on photolysis suggest that photoionization is generally an inefficient process in heterocyclic molecules. Let us consider the photoionization process in more detail. The direct photoionization of a neutral, molecule A

$A + h\nu \rightarrow A^+ + e^-$

As unexpected under these experimental conditions since the gas phase

ionization potentials may be greater than 8 eV. Photoionization can be

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produced by the biphoton path

$A + 2h\nu \rightarrow A^+ + e^-$

we Ma

ave ϕ_{A^*} ?

where A^* is a long lived excited state (probably a triplet), ϕ_{A^*} is the quantum yield for its formation, I_0 is the intensity of light absorbed by

A, T is the Lifetime of A^* , I_a is the intensity of Light absorbed by A ,
 ϕ the quantum yields for formation of A^* and A^+ , I_e, E_r, c, a and
 l are the respective extinction coefficients, concentrations, and optical

paths for A and A^+ , we have that

$$I_g = I_a \exp(-\epsilon c l) \quad (1)$$

$$\text{and } T_g = I_e / T \exp(-\epsilon^+ c l) \quad (2)$$

In this case the exciting and ionizing photons are assumed to have the same

energy, but similar arguments can be made for different photon energy:

the primary energy requirement is now that $h\nu \geq (I.P. - E^*)$ where $I.P.$ is

the condensed phase ionization potential, and E^* the 0-0 energy of the excited

states. Applying the steady state approximation and the (easily met) condi-

tion that the concentration of A is so large that the term $\exp(-\epsilon c l) = 0$ gives

the rate of formation of A^+ as

$$4(R^+ / a) = \text{function of } (I_e \epsilon^+ c l / \epsilon c l) \quad (3)$$

A computer program has been prepared which carries out this calculation for

various values of the input parameters. Using the data of Meyer and Albrecht?

for the photoionization of N,N,N',N Tetranethyl-p-phenylenedianine (FD)

gave good results. Thus, @ rationale is provided for the interpretation of

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?the results. The low efficiency of photoionization of the heterocyclic

molecules tested may be due to insufficient photon energy, or insufficient

Light intensity. It would also be the result of @ low quantum yield for

formation, a short-triplet lifetime, or a low triplet extinction coefficient,

?these factors cannot be assessed completely at present. However, it is

known that the triplet (π, π^*) lifetimes of some heterocyclics are shorter

?than those of the triplet (n, π^*) states of corresponding monocyclic

?compounds by factors of 1/1000.¹⁹

On the basis of the results, it is planned to modify the experimental

procedure to permit (1) longer irradiation times (2) use of « higher intensity

Lamp and (3) use of as low a wavelength as feasible.

Section B.- Theoretical Work

?The theoretical work has continued along the basic lines indicated

4 the previous Progress Report. As before, it is convenient to separate the results, according to the formalism used, into Molecular Orbital and Valence Bond calculations.

I, Molecular Orbital (M.O.) Calculations

The calculations currently being carried out utilize the Pariser-Parr-Pople (PPP) self-consistent field method^{®©} to calculate neutral molecule and radical spectra. The major defect of this method in the past has been the lack of justification for its use of repulsion integrals considerably (20%) over than the theoretical values. However, recent non-empirical, calculations on the excited states of the ethylene molecule^{?)} have given this sorely-needed justification, These calculations show that the reduction in the repulsion integrals between pi-electrons is necessary to account for

?4

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the reorganization of the sign-electron framework that occurs of excitation of @ pi-electron.

The technique used here, in the spirit of the original Pariser-Parr

method, is to search for the set of reasonable parameter values which give the best accord with the experimental singlet-singlet and singlet-triplet excitation energies of the neutral heterocyclic molecule. The same parameter values are then carried over unchanged to the calculation of the doublet-doublet excitation energies of the radical anion and radical cation of the same molecule. Such parameter searching is extremely time-consuming, but the initial results appear to justify this approach. The earlier computer program to carry out the PEP calculations on an IBM 1230 computer has been considerably refined, and a version now exists for the IBM 360 which will permit calculations on more complicated molecules. In particular, the PPP program is now linked on demand directly to Configuration Interaction (CI) program described below.

The first molecule which has been carried through the full optimization procedure is pyrrole. These results were obtained after about 20 calculations, and supersede those reported in PRIC 99. The optimized parameters and the results obtained for pyrrole, pyrrole radical cation and pyrrole radical anion are compared with the experimental results in Table 7. The agreement between the theoretical transitions of the radical cation and the experimental values assigned earlier in this report is extremely good. The actual classification of the doublet transitions and the calculation of the doublet transition energies is discussed later.

The results obtained to date for pyridine and its radical anion and cation are reported in Table 8. Calculations have been made on pyridine and the pyridine radical anion previously by Hopton and Tush. For comparison,

their results are also shown in the Table. The calculations made by Hopton

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and Hush differ in several important aspects from those reported here. Thus input Huckel wavefunctions for benzene were used, instead of the Huckel wavefunctions for pyridine used in the present work. A simplification was made by Hopton and Hush to the elements of the Hamiltonian Matrix which partly ignores the effect of electronic polarization. This simplification has not been made here. Finally, no attempt was made by Hopton and Hush to optimize the parameters used. The results in the table indicate that we obtain significantly better agreement between the theoretical and experimental transitions of pyridine. More importantly, a very much better accord is obtained for the pyridine radical anion spectrum, as measured by Hopton and Hush. The results obtained for the pyridine radical cation are also in excellent accord with the assignment made earlier in the experimental section. A similar improved accord is found between our calculations and the experimental transition energies of the pyrimidine radical anion (Table 9).

Table 10 lists the results of a calculation made on the cyclopentadiene molecule, for comparison with the valence-bond calculation. The results are in excellent accord with the experimental singlet and triplet transition:

The effect on the calculated singlet-singlet, singlet-triplet, and doublet-doublet excitations of introducing a limited amount of configuration interaction is now being studied. For the singlet and triplet states, configuration interaction is included among the excited configurations $m \rightarrow m+1$, $m \rightarrow m-1$, $m \rightarrow m+2$, $m \rightarrow m-2$, $m \rightarrow m+1$, and $m \rightarrow m-1$, where m is the highest doubly occupied orbital. No interaction terms arise between singlet and triplet excited configurations. The expressions for the singlet and triplet configuration interaction matrix elements are

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Diagonal Elements (Since the ground state energy is subtracted from each for convenience, these correspond to the excitation energies to the various states).

$$[s(s+3)/w/s(i-og)] = 5 - e_g + 2(45/43) - (44/35)$$

$$(x_{iss}/y_{24-05}) = e_s - e_g \sim (44/55)$$

where e_s and e_g are the calculated eigenvalues, and $(1/13)$ and $(44/43)$ are molecular repulsion integrals in the customary notation, that is,

2

$$3/33 = (4a) (21/2 / u_j(a)_n, (2))$$

2

$$\text{and } (38/35) \text{ } \odot \text{ (a } Q_a, (2)/S? /o3(2)u_j(2))$$

ie

ed here

for molecular orbitals u_i . Since the molecular orbitals are expressed

as linear combinations of atomic orbitals, the molecular repulsion integrals are given as a linear combination of the atomic repulsion integrals used as

input to the PPP program.

off-diagonal Elements

$$G_{li95}/e/s(s?a) = 2(45/n) - (44/52)$$

$$[P_{ag}]/\{re_a\} = -(0x/32)$$

These expressions are identical to those given by Pople.

For the CI matrix of the doublet states, the ground and excited states

were represented by the determinantal functions:~

$$(2q) = \det (u_i, o_+, u_j Q_y u_i) \text{ ism.}$$

$$(2/2/3) \sim (6/8/6) = e_y = e_y + 065 (w/a) + 045 (ifn) \sim (m/e)$$

$$(34/3/3!) - (6/3/s) = 0 = 6, + 045 (om/om) + 045 (afm) \sim (x_n/12)$$

$$(Cfife) = (Gfa/c) = e, = e_g + 2(4K/iK) = (44/xx)$$

ofe-atagonar

$$(s/t) = 0.5 (Am/em)$$

$$(At/a/a) = 0.5 (tn/rm)$$

$$(3/3/s) = 0.5. (12/2)$$

$$(B'/8/) = 0.5 (1m/mm)$$

$$(c/w/\phi) = 0.0$$

$$(ar/i/a) = 0.5 (tm/im) = (n4/mm)$$

$$(B'/tf/a) = (32/mx)$$

$$(B'/\neq/a) = (t0/ma)$$

$$o/efa) = (2M?) F(ae/sm) + 0.25 (aa/nk) \sim 0.5 (44/m) 7$$

$$(B/H/A") = (tm/mic)$$

---Page Break---

$$(Bt/iya") = (tm/ma)$$

$$(c/x/a') = (2-M2) ((1x/mm) \sim 0.5 (hi/ak) 7$$

$$(BY/H/B) = 0.5 (mk/mh) - (m/x1)$$

$$(c/a/B) = (2-M2) [(ae/mk) + 0.25 (em/mi) = 0.5 (Am/rx) 7$$

$$(cfayst) = (2^\circ) C(ax/am) \sim 045 (0/24) 7$$

?A computer program has been written to generate the singlet and triplet configuration interaction or the doublet CI matrices. The matrices are diagonalized by a standard sub-routine to give the final excitation energies. This program links directly to use the output from the PPP program,

It has been tested, and appears to work satisfactorily. This PPP-CI combination will now be employed on calculations on the diazines and their radical ions. After use on pyrrole and pyridine and their radical ions, this PPP-CE will be employed in calculations on the diazines and their radical ions,

III. Valence Bond (V.B.) Calculations

a to calculate

?These calculations use the non-empirical VB method 6 the unpaired spin states of simple heterocyclic ring systems. Initially the triplet states of cyclopentadiene and the doublet states of the cyclopentadiene radical cation are being investigated, One great advantage of the valence-bond formalism for radical calculations does not appear to have been fully exploited in the past. This is that once the necessary formalism and integrals have been derived for the parent molecule, the radical cation calculation is carried out with no additional labor by equating all integrals

involving the 'missing' electron to zero.

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4) Povmattom

ALL the possible structures for the four-electron singlet, triplet,

and quintuplet states were included} non-polar, polar and dipolar, There

structures were then expressed as a Linear combination of singlet deter-
mined basis functions. Since each basis function is a Linear combination

of atomic orbitals ϕ_j , integrals of the basis functions over the

one- and two-electron operators (\hat{H}) can be expressed as a Linear combination of atomic integrals ($\langle \phi_i | \hat{H} | \phi_j \rangle$). For cyclobutadiene there are 2 non-polar, 2 polar, and 6 dipolar singlet structures, formed from combinations of 7

aeterinantal basis functions, There are also 3 non-polar, and 12 polar

triplet structures, and 1 non-polar quintuplet state, Thun without the use of symmetry, the singlet energy levels form a 20 x 20 matrix, the triplet Levels a 25 x 15 matrix, and the quintuplet state a one-elenent 'matrix'.

However, by the use of group theory, the "structures" can be grouped into combinations corresponding to the irreducible representations of the Coy group, to vich cyclopentadiene belongs, ?This gives a 12 x 12 matrix for

the singlet A states, an 8x 8 matrix for the singlet B, states, an 8 x8 matrix for the triplet Ay states, and a7 x 7 matrix for the triplet By states.

?As stated in PRIC 99, the fomalion for obtaining these matrix elenents from

the

2 integrals (AsPA,) has been completed, It 1s not reproiuced here,

as it is voluninous,

44) Atonde Integrals

The next step is the calculation of the atomic integrals (aj)

where F is a one-electron or bi-electronic operator, or the identity opera-

tor. The integrals required in the particular formalism used are overlap

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integrals ($4/3$), repulsion integrals ($14/33$) and ($44/14$), kinetic energy

integrals ($4/2/3$), and core-attraction integrals ($11V''$) and ($45\pi^4$). 222

of these integrals were calculated using Slater orbitals with a set of

values $\zeta = 1.0$ to 2.0 in steps of 0.2 , during two months spent by

the principal investigator at the Theoretical Chemistry Center, University

of Bologna. In particular, two different forms were used for the

potential due to an sp^* hybridized C^* ion.

The Geoppert-Nayer-Sklar approximation for the latter potential

gives $V'(r^*) = V^0(r^*) - (IN f/pp)$ where V^0 represents the potential obtained

by adding an electron to the $2p$ orbital of the C^* ion, and (TW /pp) is the

repulsion between this electron and an electron in the framework of the molecule, The first method used is the usual one of assuming the electron added to a 2p orbital of a C atom, rather than a C⁺ ion, and thus using Slater orbitals throughout, The second method used here has been to employ an atomic potential derived from the self-consistent charge distributions given by Campadelli and Zauli. The potential obtained (given incorrectly in FRIC 99) is

$$V(r) = (7/2)(\exp(-12.25r) + 10.12887 + \exp(-2.588R) / + 7.8087).$$

From this potential, the form of the orbital p to be used in calculating the repulsion integral is also obtained, The appropriate integrals were calculated using the bicentric potential obtained from the Pottion equation 5 @ Linear combination of associated Legendre functions, as indicated by Tauber. -

The values of the atomic integrals calculated for the four different

atomic separations needed in the cyclopentadiene calculation, and the

a1

---Page Break---

previously mentioned parameter set, are listed in Tables 11-6. The values obtained agree very well with those reported previously for a few parameter. The present compilation is much more extensive, and the
There

values.⁷ However

2

values of the integrals are calculated to a much greater precision.

is a significant difference between the Slater and Self-consistent field approximations for the core attraction integrals in the expected direction,

that is, a larger value for the SCP integrals.

4.4.1) Basis Function Integrals

With the integrals among atomic orbitals evaluated, the integrals

($\langle \psi_A | P | \psi_B \rangle$) among determinantal basis functions ψ_A , can be calculated. This is rather tedious in sophisticated calculations, since the basis set is not assumed to be orthogonal, a serious defect of earlier work.⁹ A computer program has been written and tested by Palmieri⁹ which computes all the possible integrals ($\langle \psi_A | P | \psi_B \rangle$) over non- and bi-electronic operators, given as input the atomic integrals. This program is being used to compute a set of ($\langle \psi_A | P | \psi_B \rangle$) from each set of atomic integrals (one exponent value, one

approximation for V^*) described above.

iv) Structure Integrals

The next step consists of deriving the values for the Hamiltonian

and overlap matrix elements by substitution of the basis function integrals

into the expressions derived in part (1). The whole process of generating the 12 x 12 and 8 x 8 A, matrices, the 6 x 8 and 7 x 7 B_j matrices, and then

solving the matrix equations $[A - E\delta] = 0$ for the energy levels must

be repeated for each set of atomic integrals, or twelve times in all, A

computer program is therefore being written to carry out this procedure,

22

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using an input the (APA) value obtained from the Falnteri program. The

first part of this program, to obtain the A, states, is almost completed

23

---Page Break---

TABLE 1.

New Absorption Maxima from Gamma-Irradiated Heterocyclic
Molecules in Rigid Glasses at 77°K

Substance Glass Abs. Max. (nm) Effect of bleaching solvent

band

Silica cell 254 increase (UV bleach)

Indole Freon 1000, 620, 600, ?

565, 550

Imidazole Freon 580 decrease

Pyrazole MTHF 321 -

Pyrazole 3MP. 360, 1200 amd

Pyrrole MTHF below 400 decrease

Thiazole MTHF 330 increase

Thiophene =MTHF 370, 670 increase

Thiophene 3MP. 340, 830 decrease

---Page Break---

TABLE 2.

Absorption Maxima of Gamma-Irradiated Pyridine, Pyridazine,
and Pyrazine in MTHF Compared with Authentic Radical
Anion Spectra (Hush and Hopton)

Parent Substance Principal Absorption Maxima (nm)

Gamma-irradiation Radical Anion

Pyridine 350 335

Pyridazine 354 351

Pyrazine 340 364

---Page Break---

?wu og ye vorssjua sau e saonposd wu gz ye UONReyOxa ?uonelpess!-ewweb J9yy

?osje siskjojoyd an Aq paonposd suoissia +

cugjauosqoads g-y uJ Bulvonisod 0} anp wu gz * oy algronposdas axe xeyy

cee sey dWe = auyweyfuaydiay

az Sey ?or dwe auyWAUL

cs 4 ?sou POE dwe +s8U8N}0L

4 C62 O97 de auaydoryt

OLS ?Ces ?00S oe 06S ?Sep ?Sto AHLW auajeuuden

aun 912 Sen awe ajoushd

or ?sue oe Sop ?086 We auyzedhd

oe = = awe aulplahd

Os 062 osp We Na

OLS ?OES ?00S 00e Sib ?O6? dWE iKuaydig

ez = _ qn} BOUL!

awe

TORII wone|pedd! S521) punoduog

ayojaq XeU!

aouaosaujwiny,

LLL IE spunodwos snwore 40 2119Xs0s8)34 paye|pess! Jo (WU) .ewlXeW aouadsaU}WN}

? avi

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ssuoy3dsoaq7

Aaveeryare 908% 66 wou puUR ot JO soUNleTAD pu ZOTOO THETA ?peUFEDKD ou He 06:

SSinsodsa sognups Of 09 dn paxmibar sxouyo Tre dey of amedoxe soanupE Z a9aFe posts:

eee sr08

(1st) 3 ?008 vain ?ay 8 ssotsot99 aid ouyenphuoudtss

st) 1o9e ?805 *maD "ay *E wo0s8

(2¥61) Toe ?908 me NS uoesa motto Buo=38 rerree-tuosas -

sorteh ores

. . 80120109 e0Ts0T00 seopoTeo ? supRTMReaTAuendse

(2n6t) To9e typ "908 "HDHD EY ?Le wood (ous)

MOTTON QUSFT WoOUB-ROTTOR weasd 4uaTT supumTtuaud sd

(n96T) L6zt ?9g ?20g swat (9S foes) (Lis 625) (us *2s) sua ypousTfuaud

sbor 978 9H a TacpaaaoeToon

(ers woos

nave ?\$9 *208 sou say *e (66R) sopra quTeZ ?uaeaB-notte quyea w99a-noTTOR SUT TTUUT

ARNT

ssoTs0109 sorted ssots0T09 surrnmtaanere

(6861)

666 Soca *908 *how *o03 (62H vorrek mm (gon) eTTas Ta ssets0T00 ony

sau EAT aa Woe TABS

(11) usr 20 suoyywatosqo TensTA

HLL 9 duro ooGoeH wer89 uw BuyEn eoUTEY OTyBUDLY Jo STEKTOIOUT

4 Te

27

---Page Break---

TABLE 5

Compounds for which either no visual color was produced at 77° after 30 min. exposure to full arc of either mineralight R-5I low pressure Hy lamp or HBO 500 Osram high pressure Hg lamp, or which exhibited no color formation after purification in either MTHF, 3MP, or Freon. (Concentrations of the order 10° M or less, aerated solutions}.

Adenine

Aloxan

Barbituric acid

Benzimidazole

Furan

Hypoxanthine

Hematoporphyrin

Imidazole

Isexazole

Methyltetrahydrofuran (an impurity resulting from an oxidation of MTHF forms a blue colored intermediate)

N-methylhexylmorphine

N-cyclohexylpiperidine

N-methylpyrrole (contains an impurity which undergoes a photolytic reaction with Freon-II to produce a yellow intermediate which subsequently forms a green precipitate after warming,

N-vinylpyrrolidine

Pyrrole (see N-methylpyrrole)

Pyrolidone

Purine

Pyrazine

Pyrazole

Quinoxaline (impurity forms yellow brown-intermediate
which turns pink on warming)

Thiophene

Thiazole

s-Triazine (yellow color on warming)

Thymine

28

---Page Break---

?TABLE 6

emg rong tm nd heres tr ett

TARTS sour cour wes i eas

?or high (OSRAM HB0-500) pressure lamps Xnax reported in mi.

Sompound Matrix Conor

cmoreindcie BP +P Yellow ?

. wn Red-orange

Freon 1182 Freon Yellow (pax 370-400),

red brom color on warming

0 mur Yeuow (nsx 370-400)

Dicyelonexyithioures Freon Yellow

Indazcle vag Yellos-brom

DMP + P-L el-Yellowt

Indole Freon ?Yellor orange (neax 390, 420,

?strong and 480) yellow

precipitate on vaming

. IMP + F-IL ? Yellow-orange

. _ 00

Tsquinoline wre mlue

Te2ecycanoethylelohexyl=

?anine Freon Faint-yellow

H-2-hydroxylethyeyelohexyl-

nine Freon Yellowt

DMP + P-11 Colorless

Freon Yellow®

Quinoline DMP + P-11 Yellow

ane Pink

?Tetraphenylpyrrole Freon Yellow green (max 350, 420, 480)

Picolylanine war sl-yellow

Pyridine woe Yellow-green

Triazole (1, 2, 4) Freon Yellow

BMP + F-11 Colorles:

irr Colories:

?Triphenylindazole rr Yellow

BMP + FL Colorless

?(yellow color had a different hue from Freon 1152 color and did not yield

?a reddieh brom color on varming)«

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TABLET. PPP. Calculation on Pyrrole, Pyrrole Radical Cation, tion, and

Pyrrole Radical Anion

Parameter values optimized for pyrrole (eV)

Hy: 55-966 Hog, H55 + 38.749 H33, Hag + ~37. 990

Hen: ?7 Hee (neighbor) : -2.759 Hoc (next neighbor) : -1. 905

(NNINN) : 16.8 (CCICC): 10.4 (11/33), (11/44): 6.065

(1/22), (155) ; 8.458 (22/33), (44/55): 7.53

(22144 , (33/55) : 5.751 (33/44): 7.388 (22/55) : 5.754

Calculated and Experimental Transition Energies

Bpecies Type Transition Calculated eo Experimental (eV)

Pyrrole S-S 5.62 (! By) 5.88

19 lap 6.77

S-T 4.19 PB) 4.35

Pyrrole Radical

Cation D-D 1.16 @a) LS

3.78 (2A) 4.1(2)

Pyrrole Radical

Anion D-D 1.83 2a)

4.26 (2A)

30

---Page Break---

TABLE 8. PPP Calculation on Pyridine, Pyridine Radical Cation, and
Pyridine Radical Anion ?

Parameter values (eV)

HNN: 44.762 Ho₂, Hyg: ~41.594 H₃₃, Hess: ~42. 401

Hag: ~42.401 Hon: -2.62 Ho : -2.29

(NNINN) : 14.485 (CC/CC) : 10. 136 (11/33), (11/55): 5.61

(11/44): 3.467 (55/66), (44/55), (33/44), (22/33): 7.514

(33/66) : (22155) : 4.96 (44/66) , (33/55), (22/66), (22/44): 5.547

Calculated and Experimental Transition Energies

Calculated (eV)

Species ?Type Transition Hush & al. Present work Experimental (eV)

Pyridine S-S 5.01 5.16 4.94

5.69 5.74 6.26

6.69

7.39 7.20 1.07

S-T 4.03 3.62 3.68

Pyridine Radical

Cation D-D 1.16 a)

3.16 (2A) 3.3

3.83 (2B)

Pyridine Radical

Anion D-D 2.66 2.58 8)

4.02 (A) 37

5.26 4.17 PA)

5.03 5.16 (2C) 5.08

---Page Break---

TABLE 9. PPP Calculation on Pyrimidine, Pyrimidine Radical Cation,
and Pyrimidine Radical Anion

Parameter values (eV)

Hy: 51-319 Hyp 2 ~42,300

Hag, Hog : ~42.142 H55 : ~41.904

Hen: -2.620 Hee: -2.290

(NNINN) : 14.485 (CCICC) : 10.136

(1M/22), (22/33), (33/44), (166) : 7.777

(1/33) = 10.605 (11/44), (33/66) : 5.630

(22/44), (22/66), (44/66) : 4.965 (11/55), (33/55) : 4.995

(22/55) : 5.560 (44/55), (55/66) : 7.549

Calculated and Experimental Transition Energies

Calculated (eV)

Species ?Type Transition Hush et.al. Present work Experimental (eV)

Pyrimidine S-S 5.28 5.69 5.08

Pyrimidine Radical

Cation D-D 2.14 a)

4.69128)

Pyrimidine Radical

Anion D-D 4.17 2a) 3.15

4522) 4.97

yun

Ree

---Page Break---

TABLE 10. PPP Calculation on Cyclopentadine

Parameter value (eV)

Hit, Hyg: -29.975 Hoo : ~32.186

Hij (neighbors): -2.29

(CCICC): U.13 (11/22), (22/33), (33/44) : 7,649

(1/33): (22/44) : 5.727 (14) : 5.439

Calculated and Experimental Lowest Transition Energies

Species ?Type Transition Calculated energy (eV) Experimental Energy (eV)

Cyclopentadiene s-S 4.39 (B) 48

---Page Break---

TABLE 11.

Cyclopentadiene Integrals Slater Exponent 1.0

?

Atom Pair

Integral ab ac ad be

(ii) 5634093. 2319934. 1936038. 5339315

(iii) - 2848168. 2010504 ©. 1901081. 2776542

(imi) - 1614363 .03921277 02088053. 14612400

gi ylom) SCF - 3330885. 2103058... 1976791 - 3196969

J Slat, 3235641. 2086678. 1963364. 3114825

(i ylon, SCF 2734945 08301713 .0661794 ? . 2529374

J

Slat. .2600742 08033911 0641755. 2493955

(ijlij) - 1113775. 0158486 01149512 09964697

34

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TABLE 12. Cyclopentadiene Integrals Slater Exponent 1.2

ee

?Atom Pal

Integral ab ac a be

(ii) 45208814. 13944601. 11013530 + 42048853

(iii) 30918567. 20803517. 19591333. 29982907

(ijfij) 083647283. 0069095417 . 0042092304 . 071626458

wt) - 15467827. 014478473. 0078541393. 13525986

awl) SCF 35405901 21469056 2031055. 33777629

Slat. 34228372 21293989 19989514. 32766310

(ij ion) SCF 25937323 055803438. 04181888. 23419474

24373324 05357447 08025845. 22047924

---Page Break---

TABLE 13. Cyclopentadiene Integrals Slater Exponent 1.4

oe

Integral aa ad te

di) - 35415127 080605853. . 060131098 32286353

cinjy 32655264 21252835 «19965604 «31536321

ip 057916581 0025536092 0013841953 047561839

cm) 13372039 0036124477 .000068387338 . 11235618

civion SF serreoiz 21728359 20349823 34880286

Stat 55357503 2547002 «20201994 «33727687

W viony oe 23238287 035192265 02477383. 20472197

- 21623010 08355378 .02369576 «19088299

TABLE 14. Cyclopentadiene Integrals Slater Exponent I. 5

Integral ab a ad be

? 27175342 .045132978 031755593 24258508

cin 33899306 21562686. 20224297. 32636192

ii) 037691626. 00086964908. -. 00041842635 029629831

Gimp 10554654 -.0022078827 -.0033196588 084520331

ai vine A 37528027 «21898746 «=. 20490010 3555258)

36084262 .21709539 «20339433. 34207371

19905056 02112947 «01396498». 17102484

jon

(ij V!9)),

WW 'Nstat. gsr2050 02002613 01328279 15819802

eno een ein aeeaSeaeseo,®em:i

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TABLE 15. Cyclopentadiene Integrals Slater Exponent 1.8

Integral ab ac ad be

« 20482366 024612487 016316314 ~ 1788885

jij) 34806234 - 21787283 . 20411631 - 33433186

(iyi) 023305323 00027725079 .00011819947 017512512

(iT) 076047551 -.0044000566 -.0040289018. 057213778

q yon - 38034371. 22008523». 20586691 = 35968552

Slat. 364go120 21820729. 20433776 = 34639035

i ve", SCF 16441334 01220078 ==. 00756836 13773877

Slat. .15074184 01150453 .00716391 «12657082

TABLE 16. Cyclopentadiene Integrals Slater Exponent 2.0

Integral ab ac ad be

(i) 15198304 013127231 0081929209. 12978918

(ili) 35484170. 21955689 - 20551644 34027938

ini) 013802622. 000083711490 ..000031581069 0099032873

utp) 049211835 -. 0045380436 -.0034970947 033738883

ti vion, SCF 3835499 22090088, - 20656137 36232739

Slat. .36686173 21900425. 20501453, = 34848960

| ion, . 13179862 «00682530 00397288 . 10764089

GV" Weiat. rzorres9 00640732 00874080 © 09837164

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Lh

2B.

19.

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ol Density

Optic

o

Regon Where 1200 MH

iof| alwach increased 350. Od.

og|

o2

v O02 004 006 0.08 O10 O12

Figure 1 - Variation of Pyridine Concentration on
the Yields of 1200 and 350 mu Absorption
Bands in MTHF (dose = 1.9×10^{21})

? +? 1200 mu absorption

==--0 === 35 mu absorption

40

---Page Break---

60

2

so}

> 40

i

= 30 4

20.

. pom~ SN

6

??

250 300? = «S80~==~«O~==~C«S~«OD BOD TOO My

Figure 2 - "Warm-up" emission spectra of irradiated purified
3MeP dose on the order of 6×10^6 ev/L.

Spectra No. 1 obtained within 30 seconds after

removal of liquid nitrogen (sensitivity
3X others)

No. 2-25 min. after lig. Ng removal

No. 3-40" "ow 4 om

No. 4-60" "ou om om

No 5-75" "om om om

(Warm-up rate essentially linear for the first
4 minutes and is approx. 20min.)

41

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?Alter Emoustve Bleach

&

« |

? ate

? me NL

Figure 3 -ESR Spectra

a) FM in silica tube

b) Evacuated silica tube

c) DM droplets prepared in air

@ Degassed FM extruded from container under

liquid nitrogen prior to ESR analysis

All doses of the order 2×10^{22} evit.

a

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APPENDIX. A

Journal of Physical Chemistry (In press)

SPECTROPHOTOMETRIC IDENTIFICATION OF GROUND STATE RADICALS PRODUCED IN A HIGH HALOGENIC GLASSY MATRIX®

A. Grimison and G. A. Simpson, Puerto Rico Nuclear Centers* and Chemists
and Physics Departments, University of Puerto Rico, Rfo Piedras, PuR.

*The Puerto Rico Nuclear Center is operated by the University of Puerto Rico
for the U.S. Atomic Energy Commission under Contract No. AT-(10-1)-1653,

ABSTRACT

The absorption spectra, dose dependence and character of the intermediates produced by gamma-radiolysis at 77°K of a 50-50 Vol. % mixture of Freon-11 (CF₃Cl) and Freon-113 (CF₃Br) have been determined,

Color centers are formed at 330 nm and 585 mμ which can be bleached

dy Light of suitable wavelengths, and which are assigned to cationic

species, The stabilization of other cationic intermediates by this matrix

is demonstrated by the detection of intermediates of several heterocyclic
additives, Identification of the following cations and their λ_{max} has been

made: thiophene (830, 520 m μ), pyrrole (800 m μ), and pyridine (380 m μ).

Presented in part to the 1967, March Meeting of the American Physical
Society, Bull. Am. Phys. Soc. 12, 423 (1967).

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vanianaa?® has discussed the usefulness of some halogenic matrices

eee

1. Shida and W, He Hontl², J. Chem. Phys. 2369 (2956)-

1. Shida and W. H. Honill, J. Chem. Phys. Wh, 4372 &%

OO

for isolation and spectroscopic identification of gamma-radiolytic

Antemediates at 77°. The matrices discussed, carbon tetrachloride and

butyl chloride, are either opaque or form cracked glasses at

Liquid nitrogen temperatures, Measurements of the absorption spectra of

these matrices requires the use of short path lengths. Therefore, high

concentration of reactant and high doses may be required to produce de-

tectable spectra of radiolytic intermediates. These limitations can be

avoided if a more transparent glassy matrix could be used, which retains

the electron trapping and positive hole stabilization characteristics
of the opaque solvents.²

Sandorfy³ has discovered that a 50:50 vol. % mixture of Freon-11

3) C. Sandorfy, Can, Spectry, 10, 85 (1965).

(C₂F₆) and Freon-113 (CF₂BrCF₂Br) forms

suitable for spectroscopic studies, This matrix is transparent up to

stable, clear glass at 77°K

3 cm, path length throughout the entire visible region to 2700 mμ.»

and 1 translucent for path Lengths up to 20 cm.

The spectroscopic properties of the intermediates produced by
radiolysis in this freon mixture (jai) have been determined, the ability
of this matrix to stabilize the intermedi. Produced by radiolysis of

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Some dissolved heterocyclic compounds have also been investigated, and is reported here.

Experimental,

The apparatus used to determine absorption spectra at $T \text{ } ^\circ\text{K}$ with the

Beckman DK1A spectrophotometer is shown in Figure 1. A brass devar holder!

4) A scaled line diagram of the devar, holder, and quartz cell is available in a Puerto Rico Nuclear Center publication, FNC No. 85, 1956

permits reproducible positioning of a rectangular quartz devar in the

sample beam of the spectrophotometer. The rectangular quartz devar has

5) K. Funsbashi, P.J. Herley, and M, Burton, J, Phys. Chem., M3, 3939 (1955).

been used previously for luminescence studies, but never described. It consists of General Electric Lamp Glass No, 204 square drawn quartz tubes attached concentrically by a ring seal and fused to quartz plates at the bottom. This design was preferred to that described by Farhatziz and Dyne® for reasons of lower signal noise from nitrogen bubbles, and flexibi-

6) Farhatziz and P, J. Dyne, AECL, No, 2113, 1964.

lity in cell path length. Optical cells of 1 cm x 1 cm square Spectracil tubing, or up to 2. cm pyrex "Lollipop" cells could be used. Most of the spectrophotometric data reported here were obtained through the use of this apparatus in the Beckman DXA. However, spectra of the individual components, which form opaque films, were usually determined in a H. 8. Martin and Co. "cold finger" device, having an optical path of 1.6 cm,

using the Cary-14 spectrophotometer. All spectra were determined in times ranging from five minutes to two hours after irradiation,

Es I. Dupont or Matheson Freons were used after purification, Freon-12 was recrystallized twice at 77°K, retaining the Liquor after half the material had solidified: Freon-114s2 was distilled twice, retaining « middle portion, the purification procedures were checked by VIC analysts. Methyltetrahydrofuran (Eastman Organic Chemicals, Co.) was passed over alumina under @ nitrogen atmosphere, and then transferred under vacuum to 4 flask containing sodium-potassium alloy and stored until needed. N,N',N''-tetraethyl-p-phenylenediamine (TMD) was liberated from its dihydrochloride by addition of NaOH, then extracted with S-nethylpentane, The solution was evaporated and the solid sublimed and stored in the dark until the preparation of solutions, Resublimation was performed if discoloration occurred on standing, All other reagents were of the highest commercial purity and were distilled or sublimed prior to sample preparation,

Degassed solutions of the indicated molar concentration were prepared by conventional vacuum techniques using the required volume of FM which had been dried over molecular sieve (Type 2X) while under vacuum.

?The dose rate was estimated using the Fricke dosimeter (the density of FU being 2.61 + .05 g/cc at 77°K) in the optical cell in a devar container. Ang water.

+ Optical bleaching was performed with a 250 watt Sylvania Quartz-rodine

Laup, using Corning color filters transmitting wavelengths greater than 4460 mJ (CS NO, 3-72) or greater than 650 mJ, (CS No. 2-64). Photolysis of DED was effected by 10 min, exposure of a sample (10^{-2} M) to an Osram HBO 500 lamp.

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Results and Discussion

On gamma-irradiation a deep violet color is produced in the films. The associated spectrum is shown in Figure 2, together with the effect of bleaching with wavelengths greater than 660 mJ. The FA bands at 330 and 585 mJ are destroyed on bleaching, after bleaching there remains a broad absorption band having a maximum at 600 mJ which is unaffected by further bleaching. Absorption at wavelengths less than 270 nm could not be determined due to the solvent cut-off, but the absorption between 270 and 300 nm increases on bleaching. No other new absorption bands are produced. The variation of the optical density at 585 nm with total dose, and with the extent of purification of the film, is presented in Figure 3. This shows the 585 nm absorption to be a linear function of the dose, and insensitive to further purification after two initial purification steps. The bands in irradiated MM are relatively stable, no obvious time dependence being observed for times up to 2 hrs. The efficiency of production of the 585 nm band can be expressed as the product of the yield per 100 eV and the extinction coefficient. The value obtained from the slope of the curve in

Figure 3 for purified FA and the dose rate is $G = 6.5 \times 10^4$ (1 en)?

(molecules/100 ev).

Bleaching the sample with light of wavelengths greater than 650 nm and thus into the tail of 585 nm band, produces only a decrease in the 585 nm band. This indicates that the color centers at 330 and 585 nm are associated with distinct entities, and that the 350 nm band extends into the region 460 nm to 650 nm. Variation of the FM composition results in variation in both the relative intensities and positions of the 330 and

585 nm bands. The absorption bands produced on gamma-radiolysis of the

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separate components at 77°K were therefore determined, although aerated

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cells then had to be used, as distinct from the FX irradiation

Freon-11, maxima are produced at 310 nm and at 535 nm, with a shoulder

at 600 nm. For Freon-11452 a maximum is produced at 360 nm. These

absorption bands were also decreased on bleaching. These results show that

the color centers in the FM are similar to, but not identical with, the

color centers observed in the separate components.

Irradiation of a 0.15 M solution of the FM in glassy MUP at 77°K results in the trapped electron band of NTHP at 1200 mÅ being decreased by 78% relative to the pure solvent. This indicates that the FM is very efficient in scavenging electrons. However, the bleachable bands cannot be assigned to speci

resulting from simple electron attachment to the F₁s

This was demonstrated by the photolysis of a solution of TMD in the F₁, an α source of low energy electrons. This photolysis produced the well-known absorption of the Wursters Blue cation, but no additional absorption resembling that observed in gamma-irradiated Mt.

In order to test the possibility that the color centers observed in the F₁ are cationic in nature, an attempt was made to observe positive charge transfer on photostimulation. A solution of TMD in the FM was gamma irradiated so as to produce both FA color centers and TMD cation absorption. But under conditions where a considerable concentration of TMA neutral molecule remained, this sample was subsequently bleached with light of wavelengths greater than 460 mμ so that only the overlapping FA color centers and IMPD cation absorptions were excited. Since the IMPD cation

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6) We Cy Meyer and A. C. Albrecht, J. Phys. Chem. 66, 1268 (1962),

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itself is inert to photostimulation, a photostimulated positive charge

migration from the FM color center to TAF neutral molecule should cause

a decrease in the FM color center, and an increase in the D:D cation

absorption, The results are shown in Figure k, Those results are consistent

with a decrease in the underlying F_i absorption, and a concomitant increase

in the [GD cation absorption, Using the known relative optical densities

of Mt absorption at 585 and 630 m/e, and that of IMPUt in the absence of

any Ft absorption, the spectrum in Fig. 6 can be resolved into its compo-

nents, Thus, it is determined that Fut has an optical density of 0.25

at 585 mμ before bleaching, and that IMF^D* has 1.16 and 1.57 od units at

the same wavelengths before and after bleaching respectively. Under the

conditions of the bleaching experiment both the 585 and the 330 mμ bands

are completely removed in the absence of any additive, If it is assumed that only the positive species giving rise to the 585 mμ band react, and that all of those species are effective in causing an increase in the TMHD* absorption, then a value of $\epsilon_{585} = 1.2 \times 10^4 / M \text{ cm}^{-1}$ is obtained using $\epsilon_{195} = 1.95 \times 10^4$ (4 ex) for merot at 585 mμ. This value may be high since the migration of cations associated with the 330 mμ band contributes to the MEDt increase, and since there is, presumably, some inefficiency in the charge transfer Process. The value may be compared with that obtained from the oscillator Strength equation,® using the approximation $f = 4.32 \times 10^{-79} \epsilon_{\text{max}} \Delta \nu$ 1/2

8) RS. Muldixen, J. Chem. Phys. J, 1s (1939).

The value of $\epsilon_{585} = 0.60 \times 10^4 \text{ cm}^{-1} \text{ M}^{-1}$ determined from the data values of

450 and 750m. Assuming an $f = 1$, given the value of $\epsilon_{585} = 2.9 \times 10^4 / M \text{ cm}^{-1}$

which is approximately two times the earlier value, and provides a rough corroboration of the order of magnitude. The use of the value of $G = 5.05 \times 10^4$ and the GE value indicates that the efficiency of production of the 585 mμ MA expected by radiation is greater than 0.1/100 e.v. The shifts observed in the maxima of the cation bands in the experiments and in MI suggest that the transitions associated with these cations are not restricted to isolated entities such as CCl_3F^* and $CF_2BrCF_2Br^*$ the transitions may involve a participation of the solvent environment with these cations via electron exchange.

On the addition of small amounts ($\sim 10^{-2}$ M) of various heterocyclic compounds to the FM and subsequent γ-radiation, the yield of the solvent bands decreased, and new absorptions were produced. The results of these experiments are shown in Table 1, It is not probable that the solutes can compete effectively with the FM itself for electron trapping, so that negative intermediates of solutes are not expected in a halogen matrix. The results suggest that competition for positive charge formation in

the matrix has occurred, and that new cationic intermediates are produced.

9) These experiments can not distinguish between a cation that is the direct result of the competition for positive charge formation, or an intermediate whose precursor is the primary cationic intermediate, For convenience the term cationic intermediates is used here.

The necessary and sufficient test for the existence of a cationic intermediate of an additive must be that not only does the additive depress the $(m)^*$ absorption, but also that on bleaching the $(FM)^*$ absorption an increase in the absorption of the intermediates is produced.

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Pyrrole, thiophene, and pyridine exhibit new absorption maxima as predicted, which increase on bleaching the solvent band. These absorptions are therefore assigned to cation intermediates of pyrrole, thiophene and pyridine. A preliminary Pariser-Parr-Pople SCF calculation,^{2°} using

10) A. Grimonia, unpublished results.

optimized parameters for the appropriate neutral molecule yielded transition energies of 1.04 and 3.45 eV for the pyrrole and pyridine radical cations respectively, against the above experimental values of 2.5 and 3.3 eV for the absorptions assigned to cationic species.

For the other additives an assignment cannot be made as readily. For Snidazole, pyrimidine, pyridazine, and pyrazine the contribution of the Antemediate 1s uncertain, due to overlap with the FM color centers, The solute intermediate absorptions decrease on bleaching, but the maxima can be obtained by suitable bleaching experiments, since the FM color centers disappear more readily, It is not certain whether imidazole gives an absorption maximum at 585 mμ or enhances the FX absorption at 585 mμ, since no residual absorption is obtained on bleaching. Furan also shows a decrease in the absorption of the intermediate on bleaching, but a new maximum is formed at 500 mμ. (The absorption of irradiated thiophene which increases on bleaching, also exhibits a new maximum at 530 mμ). A possible explanation of the decreases observed on bleaching intermediates from furan, imidazole, pyrimidine, pyrazine, and pyridazine 1s that these intermediates are photolytically unstable, the nature of these species is being further investigated,

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The glassy FA matrix is recommended for use in isolating gemma-radicalolytic intermediates because of its superior transmission properties, its ability to trap electrons irreversibly, to trap positive charges reversibly and to stabilize cationic intermediate

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Division of Blolay and

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srreo ,d08TTTOT, OIA poe ?sapTOR Tr9> ?eTToo

gqxenb axenbs ?x9pTou reap ?reKop zqrenb-

axmbs snous oxnB7i *zounqoydor300ds,

?epic wewyoeg WTA osm quomTmbes TwT}dO

°T munOLE

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OPTICAL DENSITY

FIGURE 2,

Absorption of doubly purified irradiated

50:50 v/v mixture of Freon-22 and

Freon-LIM2 at 71°K; ?after irradiation

$(26 \times 10^7 \text{ ev/2})^5$

after 20 min,

photobleaching.

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(585 M a)

OPTICAL DENSITY

10 2 30 4% 50 60 min

FIGURE 3, Optical density of irradiated 50:50 V% mixtures of Freon-11 and Freon-11482 at 585 m μ vs, time of gamma-irradiation at 4.7×10^6 ev/1 min. and 77°

© - E.I, Dupont Co, reagents; 0 - doubly

Purified reagents (Freon-11 - recrystallization;

Freon-114n2 - distillation); © - triply purified reagents,

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OPTICAL DENSITY

FIGURE 4, Absorption spectrum of irradiated

N,N, N'N' tetramethyl-p-phenylene-

@tanine (1x 10[°]? M in Fu at T1°K)

(Dose rate = 4.7 x 10[°] ev/1 mins).

? After 10 min, irradiation,

seo After 10 min, bleach (47460 mi).

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800p *T/Ao geo x Cite

emeaz09p = OHO ?EHO. 6270 aE Sys SL g0T X ate suproppsty

exvozo0p zo ero 069 OT x eT suyzeshs

eev0z099 Siro 270 069 Ot 22 our

sevaxouy o9't zlto one got ks suypTste

sevaz09p ont os povemyes ??aTorupT

emvozouy ust 6<70 cog t/t got x bz ayers

Wa ofS ery mos fasvaxouy 690 ?HT*O To oe ?org zt ey ouauorus

?whe 00s ww woz farvax09p ?0°T fOF*O. ito ?OtL ?oot 20T X 9H wemg

- - corr - - sun

puvq quaatos xeay 48 4 Mt SQ GO We 1H t9u09 antes

BuryoveTa uo prog #2MTOlgg sgerponroquy

Srtofoosaqay uF aie pxtoreoas

a

MLL LV WE CLVIaWRUT-£ NO SIALIGGY OTTORDOWSIT go stoaset

1 svn

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