PRNC-116 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 ---Page Break--- PNRC-116 (CHEMISTRY (T1D-4500) 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 ---Page Break--- Personnel. Participating: Dr. A. Grimison, Chief Scientist, Principal Investigator Dr. G. A. Simpson, Associate Scientist M. Trujillo, Graduate Student Assistant S. Quadri, IAEA Participant O. Pérez, Research Assistant (Part-time) ---Page Break--- 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 Radiolytic 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 (2MP) 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-methyl-tetrahydrofuran (MTHF) as well. This stems from our earlier observation (mic 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. In their work, the neutral heterocyclic molecules were reduced by metallic sodium in MTHF 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. ---Page Break--- 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 from 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 on the initial pyridine concentration. The 1200 nm band corresponds to the position of the trapped electron band in MTHF. 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 decreases 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 MTHP, 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 x 10■■ pyridine. However, at higher concentrations, bleaching 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 34P. 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-MTHP 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 reported (FRNC 99). At the suggestion 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 MTHP, 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, signed peaks at 850 and 520 nm, the ar,

The thiophene radical cation was pyrrole radical cation. dmax at 800 and 310 (?) nm, and the pyridine radical cation Xmax at 380 nm. in excellent accord with the Pariser-Parr-Pople calculations reported later. The results for pyrrole and pyridine are ---Page Break--- (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 Ar (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 --- induced luminescence has been observed in irradiated 3 we? and is considered 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 the luminescence to the result of either electron-cation or exciton-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 exciton in either MEP or Pi irradiated matrices. Hanill maintains (private communication) that the absence of an effect may be expected in MTHF since only anionic 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 IMDP is observed to form a colored, salt-like product on warming. Possibly recombination in this matrix involves bond formation 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 Aninco Soman Spectrophotofluorimeter using either the Aninco 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 exhibits a number of bands on excitation with light at 300, 400, and 555 nm. Light 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. ---Page Break--- 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 exciton spectra is obtained. The results for the luminescence of pure xP are in good agreement with those of the Funabashi 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, pyrazine, pyrrole, naphthalene (MIHF solvent), thiophene, toluene, and triphenylamine. The results with biphenyl and triphenylamine have been reported earlier by Hasil and Skelly. Emissions from y-irradiated toluene on warming have been observed previously by Brocklehurst et al., and from photolyzed toluene on u.v. excitation by Porter. The similarity of the thermo-luminescence emission bands of toluene following y-irradiation to those induced by u.v. excitation suggests that excitation of neutral benzyl radicals is also being produced in the thermoluminescence study. ---Page Break--- Several formulations which were obtained with illuminated silica tubes (#1) are of considerable interest. An absorption band with a clear λ 256 nm is produced on irradiation, and this band disappears on warming. Fluctuation into this band was observed to produce an emission at 310 nm. These effects are attributed to hydroxyl radicals arising from water absorbed from the surface of the silica for a number of reasons. Water is strongly absorbed on silica and it is known that hydrogen atoms are produced by radiolysis of this water, with an enhanced yield. The presence of hydroxyl radicals 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 a maximum at 260 nm in aqueous solutions. The hydroxyl radical exhibits an emission band at 306 nm in the gas.

phase2? 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 a 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 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, ---Page Break--- 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 kinetics. 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 Radical Intermediates at 77°K The principal work on electron spin resonance has been related to intermediates 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 atom 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 H2O, may be present. (See Figure 3b) ---Page Break--- 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 1 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 1 indicates that some air contamination of FA has occurred despite precautions. Bleaching experiments indicated that the principal effect of the ESR spectrum of photolyzing irradiated FA with visible light (see attached preprint for effects on the absorption spectrum) is to increase the resonances in the center portion of the spectrum, near g = 2. This can be correlated with the increase in the absorption of irradiated FA at wavelengths less than 300 nm on bleaching. The only ESR signals which decrease on bleaching are the extreme left of the spectrum (field approx. 2800 gauss and frequency 9.2 gigacycles/sec). These signals can therefore be correlated with the positively charged species in irradiated FA with absorption bands near 350 and 585 nm, which are removed by bleaching. IV. Photochemistry of Aromatic Amines and Heterocyclic Compounds at 77°K Recent evidence has demonstrated the generality of the biphotonic ionization of a large class of compounds via their triplet states. It is

Conceivable that radical cations of heterocyclic compounds can be generated in this fashion. Since neutral radicals can also be produced via simple excitation transfer, photolysis provides an independent method of establishing the nature of radiation-induced intermediates. Photolysis was carried out in 1 on square quartz cells in a square optical device with liquid nitrogen by exposing the device to the full arc of a Muneralight R-51 low pressure mercury lamp, or an Osram H20 500 high pressure mercury lamp. In order 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 1 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 methyl- aniline and ethylaniline obtained here are the first reports of steady state, opposed to flash photolysis, photolysis of these compounds. The hypothesis of Hani2i™ 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. Douzoul? 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 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 450 nm, which was assigned to a neutral radical at that time rather than the indole radical cation. The λmax observed here is at 120 nm. 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 114 can be compared with the species produced by Hanill and Bertin by γ-irradiation of methyl bromide or sec. butyl bromide in MP, and having λmax at 360 nm. A band having a similar bleaching response has also been observed in the γ-irradiation of alkyl iodides in 3MP. These bands have been assigned to the charge-transfer complex X.RK, arising from recombination of X and R. The photolyzed Freon 114 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 suggests 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+ + e- is unexpected under these experimental conditions since the gas phase ionization potentials may be greater than 8 eV. Photoionization can be 12

---Page Break--- produced by the biphoton path a+ ty OR ge we Ma ave nv Bla ats € where A* is a long-lived excited state (probably a triplet), $ is the quantum yield for its formation, Ig is the intensity of light absorbed by A, T is the lifetime of A, Ia" is the intensity of light absorbed by AM, § the quantum yields for formation of €* and AY, Ife, Er, cy ct, a and at are the respective extinction coefficients, concentrations, and optical paths for A and A¥, we have that Ig = 1, LB (-e87 and Tg! = Ie/T> Exp (-e* ot 647 In this case the exciting and ionizing photons are assumed to have the same energy, but similar arguments can be made for different photon energies; the primary energy requirement is now that hy © (I.P. - Et) 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) condition that the concentration of A is so large that the term exp (-fcd) = 0 gives the rate of formation of AY as 4(R'7 /at = function of (13 # f'erT/ec) A computer program has been prepared which carries out this calculation for 38 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, a rationale is provided for the interpretation of 13 ---Page Break--- 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 a 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 (a, f+) lifetimes of some l-heterocyclics are shorter than those of the triplet (1, 7#) states of corresponding homocyclic compounds by factors of 1/1000.19 On the basis of the results, it is planned to modify the experimental procedure to permit longer irradiation times.

(it) use of « higher intensity Lamp and (it) use of as low a wavelength as feasible. Section B.- Theoretical Work The theoretical work has continued along the basic lines indicated in 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%) lower 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 the reorganization of the pi-electron framework that occurs upon excitation of a 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 emit 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 Hush. For comparison, their results are also shown in the Table. The calculations made by Hopton 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 transitions. 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 → mel, m → amt2, mel → mel, and m-l → omt2, 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:

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

[s(so3)/w/s(i-og)] = 5 - eg + 2(45/43) - (44/35) (x(iss)/y24-05) = es - eg - (44/55)

where e1 and e2 are the calculated eigenvalues, and (1/13) and (44/43) are molecular repulsion integrals in the customary notation, that is,

(2/3) = (4a) (21/2 /uj(a)n,(2))^2 and (38/35) = (a Qa,(2)/S— /o3(2)uj(2)) is defined here for molecular orbitals u. 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(1.95)/e/s(s-a) = 2(45/n) - (44/52)

[P(a)/rea] = -(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:

a) = det (u1, o+, uyQyu,) = m, where the bar denotes beta spin, and m is the highest (singly) occupied level.

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a) = det (a, o, 8, y,) = t(m)

(a) = det(uyiy ... uyQiu,) = m to k

(am) = det(ugie + apni 0itn)

B(= m2) to m

C(3) = det a .45 uyiguy) = m to 2 (= m2)

(eo) = (2° M2)

det(ughy v2 upuicta) + det(ugy vee Uytyta)

7 4 to k use of the

Approximation of Longuevin and Pople gives rise to the following matrix elements: - Diagonal, (afta) ~ (G/8/6) = eq - e4 + 065 (nerf) + 065 (4m/im) - (44/mm) (AY/a/A") = (6/216) = 6g = ey + 065 (mn/zmn) + 0.5 (t/t) = (n/m) (2/2/3) ~ (6/8/6) = ey = ey + 065 (w/a) + 045 (ifn) ~ (m/e) (34/3/3!) - (6/3/s) = 0 = 6, + 045 (om/om) + 045 (afm) ~ (xn/12) (Cfife) = (Gfa/c) = e = eg + 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/¢) = 0.0 (ar/i/a) = 0.5 (tm/im) = (n4/mm) (B/tf/a) = (32/mx) (B'/¥/a) = (t0/ma) o/efa) = (2M?) F(ae/sm) + 0.25 (aa/nk) ~ 0.5 (44/m) 7 (B/H/A") = (tm/mic) ---Page Break--- (Bt/iya") = (tm/ma) (c/x/a') = (2-M2) ((1x/mm) ~ 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°) C(ax/am) ~ 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 subroutine 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-CI will be employed in calculations on the diazines and their radical ions, IIT. Valence Bond (V.B.) Calculations to calculate ‘These calculations use the non-empirical VB method for 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. 19 ---Page Break--- 4) Povmattom ALL the portable structures for the four-electron singlet, triplet, and quintuplet states were included; non-polar, polar, and dipolar. These structures were then expressed as a linear combination of singlet determinant basis functions Ay. Since each basis function Ay is a linear combination of atomic orbitals aj, integrals of the basis functions over the one- and two-electron operators (AyFA,) can be expressed as a linear combination of atomic integrals (a,P4). For cyclohexane, there are 2 non-polar, 22 polar, and 6 dipolar singlet structures, formed from combinations of 7 determinant basis functions. There are also 3 non-polar and 12 polar triplet structures, and 1 non-polar quintuplet state. Thus, 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-element matrix. However, by the use of group theory, the "structures" can be grouped into combinations corresponding to the irreducible representations of the point group to which cyclopentadiene belongs. This gives a 12 x 12 matrix for the singlet A states, an 8 x 8 matrix for the singlet B states, an 8 x 8 matrix for the triplet A states, and a 7 x 7 matrix for the triplet B states. As stated in PRIC 99, the formulation for obtaining these matrix elements from the two integrals (AsPA,) has been completed. It is not reproduced here, as it is voluminous. 44) Atomic Integrals The next step is the calculation of the atomic integrals (aja) where F is a one-electron or bi-electronic operator, or the identity operator. The integrals required in the particular formalism used are overlap integrals (4/3), repulsion integrals (14/33) and (44/14), kinetic energy integrals (4/2/3), and core-attraction integrals (11V") and (45¥"4). 222 of these integrals were calculated using Slater orbitals with a set of values from k = 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 formulations were used for the potential due to an sp* hybridized c* ion. The Geoppert-Nayer-Sklar approximation for the latter potential gives V'(or*) = V°(ep") ~ (IN f/pp) where V° 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 π 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 a potential derived from the self-consistent charge distributions given by Campadelli and Zauli. The potential obtained (given incorrectly in FRIC 99) is ve(sp?) = (7)(Exp (-12.25n) & + 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 Potton 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 previously mentioned parameter set, are listed in Tables 11-6. The values contained agree very well with those reported previously for a few parameters. The present compilation is much more extensive, and the values. However, the values of the integrals are calculated to a much greater precision. There 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. Basic Function Integrals With the integrals among atomic orbitals evaluated, the integrals (AyPAs)

A set of determinantal basis functions 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. A computer program has been written and tested by Palmieri, which computes all the possible integrals (A, PA) over mono- and bielectronic operators, given as input the atomic integrals. This program is being used to compute a set of (A, F) from each set of atomic integrals (one exponent value, one approximation for V*) described above.

‘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 matrices, and then solving the matrix equations |i7 - |& 7/8| = 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, using as input the (A, P) values obtained from the Palmieri program. The first part of this program, to obtain the A states, almost completes.

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 and	
Pyrrole	MTHF	below 400	decrease
Thiazole	MTHF	330	increase
Thiophene	MTHF	370, 670	increase
Thiophene	3MP.	340, 830	decrease

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

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vorssjua sau e saonposd wu gz ye UONReyOxa “uoneIpess!-ewweb J9yy “osje siskjojoyd an Aq paonposd suoissiua + 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 snewore 40 2119Xs0s8)34 paye|pess! Jo (WU) .ewIXeW aouadsaU}WN} € avi ---Page Break--- ssuoy3dsoaq7 Aaveeryare 908% 66 wou puUR ot JO soUNIeTAD pu ZOTOO THETA “peUFEDKD ou He 06: SSinsodsa sognups Of 09 dn paxmibar sxouyo Tre dey of ameodxe 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 Hematophorphyrin Imidazole Isexazole

Methyltetrahydrofuran (an impurity resulting from an oxidation of MTHF forms a blue colored intermediate) N-methylhexylmorphine N-cyclophexylpiperidine 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. Compound Matrix Conor cmoreindcie BP +P Yellow — . wn Red-orange Freon 1182 Freon Yellow (pax 370-400), red brom color on warming 0 mur Yellow (nsx 370-400) Dicyclohexylthiourea Freon Yellow Indazole vag Yellow-brom DMP + P-L el-Yellowt Indole Freon ‘Yellow orange (neax 390, 420, ‘strong and 480) yellow precipitate on warming . IMP + F-L — Yellow-orange . _ oo Tsoquinoline were mlue Te2ecyclohexylethylamine Freon Faint-yellow H-2-hydroxyethylcyclohexylamine Freon Yellowt DMP + P-11 Colorless Freon Yellow® Quinoline DMP + P-11 Yellow and Pink ‘Tetraphenylpyrrole Freon Yellow green (max 350, 420, 480) Picolylamine war sl-yellow Pyridine woe Yellow-green Triazole (1, 2, 4) Freon Yellow BMP + F-11 Colorless irr Colorless: ‘Triphenylimidazole rr Yellow BMP + FL Colorless ‘(yellow color had a different hue from Freon 1152 color and did not yield ‘a reddish-brown color on warming)« 29 ---Page Break--- TABLET. PPP. Calculation on Pyrrole, Pyrrole Radical Cation, 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
Species Type Transition Calculated e_o Experimental (eV)
Pyrrole S-S 5.62 (1) 5.88
S-T 4.19 (1) 4.35
Pyrrole Radical Cation D-D 1.16 (1) 3.78 (2A) 4.1 (2)
Pyrrole Radical Anion D-D 1.83 (2) 4.26 (2A)
---Page Break---
TABLE 8. PPP Calculation on Pyridine, Pyridine Radical Cation, and Pyridine Radical Anion — Parameter values (eV)
H_NN: 44.762
H_o2, H_yg: ~41.594
H_33, H_ess: ~42.401
H_ag: ~42.401
H_on: -2.62
H_o: -2.29
(NN/NN): 14.485
(CC/CC): 10.136
(1/33), (1/55): 5.61
(1/44): 3.467
(5/66), (4/55), (3/44), (2/33): 7.514
(3/66): 4.96
(4/66), (3/55), (2/66), (2/44): 5.547
Calculated and Experimental Transition Energies
Calculated (eV)
Species Type Transition Hush et 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
S-T 4.03 3.62 3.68
Pyridine Radical Cation D-D 1.16 (1) 3.16 (2A) 3.3 3.83 (2B)
Pyridine Radical Anion D-D 2.66 2.58 (1) 4.02 (A)

3 5.26 4.17 (1) 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)
H_y: 51.319
H_yp: ~42.300
H_ag, H_og: ~42.142
H_55: ~41.904
H_en: -2.620
H_ee: -2.290
(NN/NN): 14.485
(CC/CC): 10.136
(1/22), (2/33), (3/44), (16): 7.777
(1/33): 10.605
(1/44), (3/66): 5.630
(2/44), (2/66), (4/66): 4.965
(1/55), (3/55): 4.995
(2/55): 5.560
(4/55), (5/66): 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 (1) 4.69 (2)
Pyrimidine Radical Anion D-D 4.17 (2) 3.15 (4) 4.97
---Page Break---
TABLE 10. PPP Calculation on Cyclopentadine
Parameter value (eV)
H_it, H_yg: -29.975
H_oo: ~32.186
H_ij (neighbors): -2.29
(CC/CC): 1.13
(1/22), (2/33), (3/44): 7.649
(1/33): (2/44): 5.727
(1) : 5.439
Calculated and Experimental Lowest Transition Energies
Species Type Transition Calculated energy (eV)

Experimental Energy (eV) Cyclopentadiene s-S 4.39 (B) 48 ST 2.18 PB) 31 ---Page Break--- TABLE 11. Cyclopentadiene Integrals Slater Exponent 1.0 — Atom Pair Integral ab ac ad be (il) 5634093. 2319934. 1936038. 5339315 (ili) - 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 ---Page Break--- TABLE 12. Cyclopentadiene Integrals Slater Exponent 1.2 ee ‘Atom Pal Integral ab ac a be (il) 45208814. 13944601. 11013530 + 42048853 (ili) 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 ---Page Break--- 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 ---Page Break--- Lh 2B. 19. REFERENCES 3. Mc Dodd, F, J, Hopton and W. $. Hush, Proc. Chem. Soc., 62 (1962). Ph.D. Thesis, P. J. Hopton, University of Bristol, 1962. H. I. Josheck and L. I. Grossweiner, J. Am. Chem. Soc. 82, 3261 (196). ©. Jangeen and K, Funcbasht, J. Chem. Phys. 45, 101 (1967) and references therein. D. Ws Skelly and W. He Hani, J. Chem. Phys. 43, 3497 (1955). B. Brockelhurst, F. D, Russell and M. I. Savadatti, Trans. Faraday, Soc. 62, 1129 (1956). W. A, Gibbon, G. Porter, and M. I. Savadatti, Nature 205, 1355 (1955). Re Livingston, H. Zeldes, and E. H, Taylor, Diss. Faraday Soc., 19, 166 (2955). M. A. Krohn, Chem. Tech. Division, Ann. Prog. Rept. May 31, 1956 ORL 3945, F215-220. Js XK, Thomas, et al., J. Phys. Chem. 10, 2409 (1966). J. Calvert and J, Pitts, Photochemistry, p. 202, John Wiley (1956). C. Reid, J. Chem. Phys. 21, 1806 (1953). K. Kondo, Ms Ry Ronayne, J. P. Guarino and W. He Hardil, J. Am. Chem. Soc. 85, 1257 (1964). G. Helene, R. Santus and P. Douzou, Photochem. and Photobiol. 5, 127 (2966). L. I. Grossweiner and W. A, Mulacy Rad, Res. E, P. Bertin and W. H. Hamill, J. Am. Chem. Soc. 86, 1501 (1964). J. Py Mittal and W. H. Hamill, J. Am.

Chem. Soc. 89, 5749 (1967). K. Watanabe, T. Nakagawa, and J. Mottl, U.S. Dept. Comm., NBS FB-158-317 (1959). W. C. Meyer and A. C. Albrecht, J. Phys. Chem. 65, 1268 (1962). 20, 515 (1959). K. Lover and M. A. El-Sayed, Chem. Rev. 65, 199 (1966). 38 ---Page Break--- 20. R. G. Parr, ‘The Quantum Theory of Molecular Electronic Structure’, W. Benjamin, New York (1969). Electronic Structure. D. Dunning and V. McKoy, J. Chem. Phys. 87, 1735 (1967). 22. J. A. Pople, Proc. Phys. Soc. (London) 463, 61 (1955). 28. C. Longuet-Higgins and J. A. Pople, Proc. Phys. Soc. (London) 68, 1 (1955). C. Daudi, J. Chem. Soc. 2204 (1960). 25. F. Caprilelli and C. Zauli, Theor. Chim. Acta (Berlin) 6, 260 (1956). 2. G. Es Tauber, J. Chem. Phys. 29, 300 (1959).

Computer program written by P. Bernardi, University of Bologna. 21. I. Savini, Thesis 1955, University of Bologna; A. Mangini and C. Zauli, J. Chem. Soc. 2210 (1950). 28. G. Pane, B. Tesini, Ind. Bologna 2, 155 (1966). 3. C. Slater, Rev. Mod. Phys. 25, 199 (1955). 30. P. Palmieri, University of Bologna, private communication. 39 ---Page Break--- ol Density Optics Region Where 1200 nm of light increased 350 nm. Figure 1 - Variation of Pyridine Concentration on the Yields of 1200 and 350 nm Absorption Bands in MTHF (dose = 1.9 x 10^21) — +— 1200 nm absorption =--0 === 350 nm 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 x 10^8 eV/L. Spectra No. 1 obtained within 30 seconds after removal of liquid nitrogen (sensitivity 3X others) No. 2-25 min. after liquid N2 removal No. 3-40" "ow 4 om No. 4-60" "om om om No. 5-75" "om om om (Warm-up rate essentially linear for the first 4 minutes and is approx. 20 min.) 41 ---Page Break--- ‘Alter Emissive 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 x 10^22 evit. a ---Page Break --- APPENDIX. A Journal of Physical Chemistry (In press) SPECTROPHOTOMETRIC IDENTIFICATION OF GAMMA-RADIOLYTIC INTERMEDIATES IN A NEW HALOGENIC GLASSY MATRIX® Mars A. Grimison and G. A. Simpson, Puerto Rico Nuclear Center* and Chemistry and Physics Departments, University of Puerto Rico, Río Piedras, P.R. 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-T (CCl3F) and Freon-11 (CBrF3) have been determined. Color centers are formed at 330 nm and 585 nm which can be bleached by 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 λmax has been made: thiophene (830, 520 nm), pyrrole (800 nm), and pyridine (380 nm). Presented in part to the 1967, March Meeting of the American Physical Society, Bull. Am. Phys. Soc. 12, 423 (1967). 43 ---Page Break --- Vania? has discussed the usefulness of some halogenic matrices. 1. Shida and W. H. Honl, J. Chem. Phys. 24, 2369 (1956). 1. Shida and W. H. Honl, J. Chem. Phys. 25, 4372 (1956) for isolation and spectrophotometric identification of gamma-radiolytic intermediates 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 require the use of short path lengths. Therefore, high concentrations of reactant and high doses may be required to produce detectable 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. Sandorfy has discovered that a 50:50 vol. % mixture of Freon-11 (CCl3F) and Freon-12 (CF2BrCF2Br) forms a suitable matrix for spectroscopic studies. This matrix is transparent up to stable, clear glass at 77°K and has a path length throughout the entire visible region to 2700 nm and is translucent for path lengths up to 20 cm. The spectroscopic properties of the intermediates produced by radiolysis in this freon mixture have been determined, and the ability of this matrix to stabilize the intermediates produced by radiolysis of some dissolved heterocyclic compounds has also been investigated and is reported here.

Experimental: The apparatus used to determine absorption spectra at 77°K with the Beckman DKIA spectrophotometer is shown in Figure 1. A brass dewar holder permits reproducible positioning of a rectangular quartz dewar in the sample beam of the spectrophotometer. The rectangular quartz dewar has 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 Farhataziz and Dyne for reasons of lower signal noise from nitrogen bubbles and flexibility 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 DKIA. However,

spectra of the individual components, which form opaque films, were usually determined in a H. B. Martin and Co. “cold finger" dewar, having an optical path of 1.6 m, using the Cary-14 spectrophotometer. All spectra were determined in times ranging from five minutes to two hours after irradiation. E. 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-114 was distilled twice, retaining a middle portion. The purification procedures were checked by VC analysts. Methyltetrahydrofuran (Eastman Organic Chemicals, Co.) was passed over alumina under a nitrogen atmosphere, and then transferred under vacuum to a flask containing sodium-potassium alloy and stored until needed. N,N',N''-tetramethyl-p-phenylenediamine (TMD) was liberated from its dihydrochloride by addition of NaOH, then extracted with n-methylpentane. 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/cm^3 at 77°K) in the optical cell in a dewar containing water. Optical bleaching was performed with a 250 watt Sylvania Quartz-iodine lamp, using Corning color filters transmitting wavelengths greater than 460 nm (CS No. 3-72) or greater than 650 nm (CS No. 2-64). Photolysis of DED was effected by 10 min exposure of a sample (10^{-5} M) to an Osram HBO 500 lamp. Results and Discussion On gamma-irradiation a deep violet color was produced in the films. The associated

spectrum is shown in Figure 2, together with the effect of bleaching with wavelengths greater than 560 nm. The FA bands at 330 and 585 nm are destroyed on bleaching. After bleaching, there remain a broad absorption band having a maximum at 600 nm 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 FA, 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 FA 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 Γ = 8.5 x 10 (1 eV)? (molecules/100 eV). Bleaching the sample with light of wavelengths greater than 650 nm and thus into the tail of the 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 FA composition results in a variation in both the relative intensities and positions of the 330 and 585 nm bands. The absorption bands produced on gamma-radiolysis of the separate components at 77°K were therefore determined, although aerated cells then had to be used, as distinct from the FX irradiation. For Freon-11, maxima are produced at 310 nm and at 535 nm, with a shoulder at 600 nm. For Freon-114, 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 Vf solution of the FM in glassy MUP at 77°K results in the trapped electron band of NTHP at 1200 mA 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 species resulting from simple electron attachment to the FM. This was demonstrated by the photolysis of a solution of TMD in the FM, an source of low energy electrons. This photolysis produced the well-known absorption of the Wurster's Blue cation, but no additional absorption resembling that observed in gamma-irradiated MUP. In order to test the possibility that the color centers observed in the FM 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 molecules remained. This sample was subsequently bleached with light of wavelengths greater than 460 nm so that only the overlapping FA color centers and TMD cation absorptions were excited. Since the TMD cation (see Meyer and A. C. Albrecht, J. Phys. Chem. 66, 1268 (1962)), itself is inert to photostimulation, a photostimulated positive charge migration from the FM color center to TMD neutral molecules should cause a decrease in the FM color center, and an increase in the TMD cation absorption. The results are shown in Figure 4. Those results are consistent with a decrease in the underlying FM absorption, and a concomitant increase in the TMD cation absorption. Using the known relative optical densities of MUP absorption at 585 and 630 nm, and that of TMD in the absence of any FM absorption, the spectrum in Fig. 6 can be resolved into its components. Thus, it is determined that TMD has an...

optical density of 0.25 at 585 nm before bleaching, and that IMFD* 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 nm bands are completely removed in the absence of any additive. If it is assumed that only the positive species giving rise to the 585 nm band react, and that all of those species are effective in causing an increase in the TMHD* absorption, then a value of ε585 = 1.2 x 10^4 M^-1 cm^-1 is obtained using ε #195 x 10^4 (4 ex)" for merit at 585 nm. This value may be high since the migration of cations associated with the 330 nm 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 x 10^7 ε max Δν 1/2. The value of Δν = 0.60 x 10^-2 cm^-1 is determined from the data values of 450 and 750 nm. Assuming an f = 1, given the value of ε 585 = 2.9 x 10^4 M^-1 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 ε 505 = 1.2 x 10^4 and the GE value indicates that the efficiency of production of the 585 nm MA expects by radiation is greater than 0.1/100 eV. The shifts observed in the max of the cation bands in the components and in MI suggest that the transitions associated with these cations are not restricted to isolated entities such as CCl3F* and CF2BrCF2Br*. The transitions may involve a participation of the solvent environment with these cations via electron exchange. On the addition of small amounts (~+ 10^-2 H) of various heterocyclic compounds to the FM and subsequent UV irradiation, 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, 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. These experiments cannot 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. ---Page Break--- Pyrrole, thiophene, and pyridine exhibit new absorption maxima as indicated, which increase on bleaching the solvent band. These absorptions are therefore assigned to cationic intermediates of pyrrole, thiophene, and pyridine. A preliminary Pariser-Parr-Pople SCF calculation, using 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 intermediate is 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 indazole gives an absorption maximum at 585 nm or enhances the FX absorption at 585 nm, 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 nm. (The adsorption of irradiated thiophene which increases on bleaching, also exhibits a new maximum at 530 nm). A possible explanation of the decreases observed on bleaching intermediates from furan, imidazole, pyrimidine, pyrazine, and pyridazine is that these intermediates are photolytically unstable, the nature of these species is being further investigated. ---Page Break --- The classy FA matrix is recommended for use in isolating gamma-radiolytic intermediates because of its superior transmission properties, its ability to trap electrons irreversibly, to trap positive charges reversibly, and to stabilize cationic intermediates. Acknowledgement The authors wish to thank Professor C. Sendorfy for suggesting this matrix, and Professor W. H. Hastil for much helpful discussion. This Division of Biology and 52 ---Page Break --- srreo, d08TTTOT, OIA poe ‘sapTOR Tr9> ‘eTToo gqxenb axenbs ‘x9pTou reap “reKop zqrenb- axmbs snous oxnB7i *zojounqoydor300ds, ‘epic wewyoeg WTA osm quomTmbes TwT}dO °T munOLE ---Page Break --- OPTICAL DENSITY FIGURE 2, Absorption of doubly purified irradiated 50:50 V% mixture of Freon-22 and Freon-LIM2 at 71°K; —after irradiation (26 x 10^7 ev/2) after 20 min, photobleaching. 54 ---Page Break --- (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 nm vs, time of gamma-irradiation at 4.7 x 10^6 ev/1 min. and 77° C - E.I. Dupont Co, reagents; 0 - doubly purified reagents (Freon-11 - recrystallization; Freon-114n2 - distillation); © - triply purified reagents, 55 ---Page Break --- OPTICAL DENSITY FIGURE 4, Absorption spectrum of irradiated ‘N,N,N'N' tetramethyl-p-phenylene- diamine (1 x 10^-7 M in Fu at T1°K) (Dose rate = 4.7 x 10^6 ev/1 min). — After 10 min, irradiation, see After 10 min, bleach (47460 ml). 56 ---Page Break --- 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

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