PRNC128

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PUERTO RICO NUCLEAR CENTER

MATRIX ISOLATION STUDIES OF THE GAMMA RADIOLYSIS OF HETEROCYCLIC MOLECULES

Progress Report 4

April 1969

OPERATED BY UNIVERSITY OF PUERTO RICO UNDER CONTRACT

NO. AT (40-1)-1833 FOR U. 5. ATOMIC ENERGY COMMISSION.

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PRNC-128

CHEMISTRY (T1D-4500)

PUERTO RICO NUCLEAR CENTER

MATRIX ISOLATION STUDIES OF THE GAMMA RADIOLYSIS OF HETEROCYCLIC MOLECULES

Progress Report 4

A. Grimison and G. A. Simpson

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PERSONNEL PARTICIPATING

Dr. A, Grimison, Chief Scientist, Principal Investigator

Dr. G. A. Simpson, Associate Scientist

M, ?Trujillo Sdnchez, Graduate Student Assistant

F. Bernasconi, Graduate Student Assistant

0. Pérez, Research Assistant (Part time)

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aaa

?The results achieved in this project fron May 1966 to April 196g, were previously presented in Technical Progress Reports No. 1 (FRNC No. &8), No. 2 (ERNC No. 99) and No. 3 (PRC No. 126), The present Technical Progress Report reviews the results obtained in the period fron April. 1968, to April 1969, the tine of preparing this Report. As has been done previously, the report is divided into tvo sections, Experimental ant Theoretical.

Section A. Experimental Results

I. General Procedures

Purification of solvents, such as 2-nethyltetrahydrofuren (MTP) or 3-nethy2pentane (34F) have been described previcusly.4%P?° ALL compounds used were of highest comercial purity. Absorption spectra were obtained as before.

Visual observations of either high or low temperature irradiated compounds were made in a darkened rom after suitably dark adapting the observers eye. Quantitative measurenents of relative themoluminescent Antensities were obtained with a comercial instrument, the Con Red ?Thermoluminescent detector, under nitrogen purging to minimize coubustion, No evidence of combustion was found, ?The device is calibrated in terms of rad-equivalents of LiF thermoluminescence, Thus, absolute comparison are possible.

ESR measurements were performed both with the Varian 4500 at IVIC, Venezuela, and vith the Varian E-3 of the Chemistry Department, U.P.R.

Estinations of "spin" concentration were made in terms of the rated instrament sensitivity 10° spins/eauss.

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A description of the experimental conditions for observing luninescence effects is found in Figures 3, 4 end 5 along with detailed list of components in Table 2. A discussion of their applications can be found in the Section "Phototonization of Heterocyclics at 77°K'

II, Absorption Spectra of Radiolytic Intermediates at T7°K

?A copy of @ paper submitted to the Journal of Physical Chemistry 4s found in Appendix 1, This paper, entitled "Electron Attachent by Pyridine and the Diazines in Gama-Radiolysis at 77°K", represents @ finalization of studies revealed in previous Technical Progress Reports.

Electron attactment in these compounds has been observed following gama radiolysis in MIF glassy solutions. This observation has been confimed by studies of bleaching effects, solvent concentration effects and through competition effects with added electron scavengers. The ?experimental spectra of anions are in excellent agreement with spectra

obtained by classical chemical procedures,

IIT. Themoluninescence Folloving Gama-Radiolysis at 77°K

Themoluninescence of irradiated biologically significant ecmpounds on waming fron 77°K has been reported previously.2?7>4 etman and Wallace? have nade extensive quantitative studies on a large mmber of compounds. Among then are adenine, having a themmoluminescence mixina at 460 m, cytosine, DNA, guanine (maxima at 510 m), thymine and uracil, Approximate estinations of the G values for themoliminescence can be made fro thelr data and are of the order 10°} photons per 100eV absorbed for adenine,

the most efficient and for uracil, 10° photons/100 ev. This technique

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is very sensitivie, with a minimum themoluninescence yield on the order 10°T photons/100 ev detected. Fleming and Kerr? have observed thermo-luminescence from adenine and cytosine with maxima near 480 nn, and vhich was identical to the crystal phosphorescence under uv exeitation,

Charlesby and Singh? nave likewise reported identifel uv induced blue Phosphorescence and thermoluminescent bands of irradiated purine and Pyrimidine bases. Thus, our visual observations of blue thermoluminescence from those compounds reported in Table 1 are in agreement both in relative magnitude and in wavelength region with the previous studies.

Studies of the phosphorescence of these compounds in aqueous solutions would place the emission bands of those campounds in the violet rather than the blue regions of the spectra, For exemple, Longworth Nes eet ee es een etree en occuring between 365 and 425 mm, and guanine at 400 nm in neutral water. Nevertheless, the fact renains that uv exeitation of the crystals produce blue entssions.2?7>4 ?Thus it may be concluded that the entities in neutral water are strongly aquated. Shifts of 50 nm may well be ascribed to strongly perturbed N-IT transitions, and can be observed in aqueous sclutions.

IV. Themoluninescence and ESR Signals after Roon Temperature Garma-Radiolys

Production of long lived free radicals in the crystalline purine

of pyrimidine bases by fonizing radiation has been observed previously, The works of Andros and Calvin,® or Cook and Eliot? provide good reference, Similarly, for those compounds irradiated at 77°K, Literature

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exists for comparative studies of both ESR and thermoluminescence of irradiated bases, viz. Sonner and Pinl.® However comparative ESR and themoluninescence studies for those compounds irradiated at room tempe~ rature have not been made, Presumeably, the existence of a high tenperature themoluminescence has not been observed.

In figures 1 and 2 ve report the ESR spectra of irradiated cytosine and uracil. ?The G values for production of those radicals are estinated to be of the order 107 and 10-3 epins/100 eV respectively. ?The radicals associated vith these unsymmetrical and unresolved spectra have g values of 2.02 and widths at half maximm intensity of less then 20 gauss. The absence of detail is characteristic of powdered samples. The g values, width and absence of large splittings suggest the presence of neutral radicals having an unpaired electrons localized on a carbon atom joined to at least one hydrogen atom, ?The similarity in the spectra of the cytosine and uracil radicals allow the suggestion that a hydrogen may have added to the carbon atans at the 4 or 5 position in the ring. This interpretation is at least consistant with the single crystal study of

Cook and Elliot,? where the presence of a radical of cytosine vith an extra H atom in the 5 position in addition to @ radical with an H atom vacancy from the nitrogen in the 3 position is reported.

In addition, the ESR spectra are sensitive to moderate heating following gamma irradiation. Heating samples of irradiated cytosine or

racil to 50°C causes a reduction in the intensity of the ESR spectr:

High temperature themmoluminescence from purine or pyrimidine bases has been observed in these laboratories. The following compounds and their

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Te

relative intensities of thermoluminescence were obtained with a conmercial

?thermoluminescence detector after irradiating to a dose of 3.5 x 109 rads:

cytosine we Taymine 13

Adenine 1s Purine 0.6

Uraci2 9.1 Guanine on

ur - 10"

All of the thermoluminescent intensities were linear in dose up to the value noted. Further, the visual observation of the temperature dependence of the luminescence places the maximum glow intensities in the range 64°C to 155°C (which were limits of temperatures at which feeble glows could be observed).

Work is anticipated to determine the quantitative aspects of the temperature dependence of both the free radical concentration and ?the thermoluminescence process. A tentative hypothesis, which we wish to test, is that the destruction of the free radical centers gives rise to the thermoluminescence, that it may be chemiluminescence, This process is distinct from that responsible for the luminescence reported in part III, which we suspect to be due primarily to recombination of ?an electron-cation pair which has stability at 77°K.

(the assistance in experimental work of Dr. H. Bemski, IvIc,

Venezuela is gratefully acknowledge).

Photoionizetion of Heterocyclics at 77°K

?A survey of the pertinent literature indicates the existence

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of same four mechanisms whereby a neutral atom or molecule may be Liberated fron a velance electron, These are:

1. Direct photoionization

2, Charge transfer to the solvent (CTTS)

3. Biphotonie photoionization

4, Lim proposal

The first mechanism is, perhaps, the most well known of the four and is the process responsible for the production of the ionisphere, On absorption of @ photon having energies greater than or equal to ?the ionization potential of the compound a cation and a separated electron are produced. Presumeably, this process can also occur in condensed phases, but the photon energy required may be lowered due to the solvation energies of the resultant ions. Since there is one to one correspondence between photons absorbed and ions produced the rate law for the overall process is linear with respect to intensity of the exciting Light.

The second mechanisn is suitable for the effect of light absorption by dons in highly polar solvents such as water, It differs from the first in that it applies to a specfic solution electronic transition - charge transfer absorption bands - and is highly influenced by temperature, solvent dielectric and the presence of added salts. It is also

@ one photon process and can be characterized by the equation.

(ion) + bh} ?5 (4on)* ?» (10n)") + emsoivatea

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This mechanism is known to occur for the halide ions, ferric salts and

Some neutral species.9

The third process may well be the most inportant for biological entities. It can provide a low energy route towards photobiclogical damage, energy storage, or conversion in biological systems. ?The mechanisn has been demonstrated to occur in aromatic amines by Albrecht, ana in aromatics by Porter. ?The mechanism requires that a long lived triplet state, initially produced by light absorption by a neutral, absorb a second photon to produce the electron-cation pair, Generally tthe photon energy required is less than half that of the gaseous donization potential. Since two photons are required the rate is a function of the square of the Light intensity.

The final mechanism, a one photon onization of the negative acridine dye ions has been proposed by Lim. The mechanism has many features in common with the CTTS mechanism and requires further experimental work to substantiate its uniquene:

Thus, the problem in denonstrating the occurrence of photo-tonization anong heterocyelics becones one of determining the appropriate mechanism of the process. In Progress Report No. 116" we have dexonstrated that sone compounds on exposure to ultraviolet Light at 77°K produced colored intermediates. We suggested that photoionization occurs in those cases. However, the procedures used were unsatisfactory in producing measurable amounts of absorbances. ?Thus, it was decided to use an altogether different approach, luminescence detection, which would be inherently more sensitive than an optical

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mer

absorption technique. Therefore, we will present our investigations of the luminescence behavior of indole, indazole, purine and tetraphenylpyrrole (riphenylemine and aniline were used as referents), The testswe employ are designed to demonstrate the occurrence of reconbination luminescence, whether it is produced in the forms of prolonged isothermal luminescence, infrared stimulated luminescence, or thermoluminescence. The time dependence of isothermal prolonged luminescence was described by Debye and Edwards? as having an intensity-tine relation of the fom I= ky, were k is a constant end proportional to the total integrated prolonged luminescence; t is time after cessation of exeiting light, and M, a mumber having an unknown dependence on concentration, being very close to unity for very low concentrations of test compound and decreasing with increasing concentration, This ?time dependence results from the diffusion controlled migration fcLlov-ing thermal excitation of trapped electrons in the fields of cationic centers in rigid media at reduced tenperatues. Skelly end Hamitl?* hhave showm that absorption of infrared light into the trapped electron absorption band causes migration of trapped electrons resulting in stimulated luminescence on reconbination with a neighboring trapped cation, Finally, Daniels! has shown that thermal stimulation by increasing temperatures causes recombination luminescence in the form of themmoluninescence. ?Typically the luminescence observed under all of these conditions is the phosphorescence of the neutral compound.

?The experimental arrangenent consisted of an intense uv light source, with appropriate filters for isolating the excitation

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wavelength, a light tight housing for the optical dear end cell, and @ high intensity grating monochromator, along with photamltipliers, Power supply, electrometer and recorders. ?The actual arrangenents are found in Figures 3, 4, and 5, with a legend of the components in Table 2. In Figure 3, the arrangement used in obtaining normal phosphorescence, fluorescence or prolonged luminescence spectra is described, Figure 4 shows the arrangement used in obtaining emissions under infrared stimulation. Finally in Figure 5 is shown the arrangement used to measure total luminescence during isothermal, infrared, or warm up stimlation of the photolyzed glassy solutions.

A denonstration of the resolution achieved by this apparatus can be found in Figure 6 where the emission spectra of benzene produced ?vy 250 mm excitation in 5MP at T7°K is demonstrated. Comparison vith data given in Pringshen?© shows the position of the maxima to be correct to within + 0.8 mm with @ resolution of 10 nm, Higher resolution is possible. The reference curve shown below the benzene emission was obtained with pure JMP and demonstrates the absence of contaminating impurities, scattered light or dewar emission, The lifetime of benzene phosphorescence was also determined as a test by shutting off the light source rapidly or flashing the General Radio Co, stroboscope and monitoring the decay on a recorder or oscilloscope. This result can be found in Figure 7. The lifetime obtained 4.7 + 0.3 sec is in good agreement with some recent vork of Kalantar??

As a further test of technique, the lifetime of the stroboscope

flash was determined. The result of this test is found in Figure 8.

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?The half intensity durations, and the decay times are measured as: low intensity, 2.7 4 sec. duration and 1.84 sec decayj med. intensitys

3.0 sec. duration and 2.2,4sec decayjand high intensity, 5.3 sec.

duration and 3.1 4 sec decay. The relative intensities of the three levels shown in Figure 8 are proportional to the actual lenp intensities

?The manufacturer quotes the duration as approximately 2 seconds shorter than those obtained here. This indicates that some undesired capacitances are present in our detection circuit. The presence of

departures from linearity in the decay plot is consistant with this.

?Thus, emission lifetimes can be measured to sone 10's of M sec with good securacy.

?The results of the luninescence measurements on indole, indazole, purine, tetraphenylpyrrole, aniline or triphenylamine in MTEF at 77° can be characterized by Figures such as No, 9 through 13, In general, if any of those compound are exposed to the full output of a high pressure mercury are for times as low as 1 second, the decay of luninescences show a time dependence similar to that found for indole in Figure 9, The overall time dependence can be expressed by the equation I= Aexp-(t/-y) +B tM, ?The departure of the curve in Figure 9 at edrly times is a result of plotting the exp-(t/,) function on a log-10g scale. Equations for the six compounds have been found for 5 second

exposures and are expressed as:

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Compound Function

Aniline T= 3.0% 10 exp-(t/4.8 + 0.3 sec)

+ 3.8 x 107M ¢-1.02 amp,

Indole I = 1.9 x 10-2 exp-(t/6.4 + 0.2 sec)

+ 1.7 x 1075 470-95

Indazole I = 6,0 x 10° exp-(t/3.5 + 0.1)

+ 3.6 x 10-6 tugh

?Triphenylemine I = 1.6 x 10-4 exp-(t/l.8 + 0.3 sec)

+ 5.0 x 10° 4-0.85

Purine I = 5.0 x 10° exp-(t/1.6 + 0.1 sec)

+ 2.8 x 10°77 48%

Tetrephenylpyrrole I = 6.3 x 107 exp-(t/1.6 + 0.2 sec)

+ 2.5 x 10-6 70.92

?The concentrations of all compounds are of the order 10-4 in mrxF, The rapidly decaying portion of the mathematical function is the normal first order decay function, and the values of ?Y obtained here agree well with the literature values where available. The prolonged luminescence is described well by the Debye-Edwards function. There is no departure from this function for a time range fran 90 seconds to at most 3 hours later when the photo mitiplier dark current is reached. There is a good correlation between the magnitude of the phosphorescence decay constants and the magnitude of the Debye-Edwards proportionality constant. That is, the greater the lifetime, the greater the prolonged luminescence, This suggest the involvenent? of the triplet state in the photoionization of these campounds.

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In figure 10 is found the emission spectra obtained during «

period fron 90 seconds to six minutes after the cessation of the exciting light for indole, indazole and aniline(with @ 40 m band pase). The spectrum obtained for indole agrees with that obtain by Freed and Sianre,!® and that of aniline with the spectrum of Lewis and Kasha?, ?Tus, es pointed out earlier, the phosphorescent state of the neutral is produced by recombination.

?The effect of infrared stimulation on the prolonged luminescence

of a 2 x 10H solution of aniline is found in Figure LL, The

effect of infrared stimulation is to change the value of the Debye-Edwards exponent from 0.8 to 1.6, This observation is consistant

with effects noted by Skelly and Hant1124 We also observe an increase in the Debye-Eavards exponent during iF stimulation of indole and indazole solutions.

?me dependence of the total reconbination luminescence on the Intensity of exciting Light is shown in Figures 12 and 15 for aniline and indole as the ratio of the square of the total exciting light intensity I ex divided by the integrated luminescence E. If a biphotonic photoionization involving the triplet state occurs, then the process can

be described by the following mechanism.

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A+nibln, at

1) ae ?e Athy!

2a A

aw + nila, at + (e7) trapped

3) at +e7 par

4) (e")erappea + heat (or hY ar) > e7

?A represents @ neutral compound, A¥ its excited triplet state, and AY ds ite cation. 9 represents the quantun yield of intersysten crossing and the product of § and Ig, the Light absorbed by the neutral, is the rate of populating the triplet state. I,' is the intensity absorbed by the triplet state. ?The trapped electron is indicated by (e")tr ande? ise free electron,

?These equations can be solved by the steady state approximation if we assume that the overall rate of repopulating the triplet state, by steps 3 and 4 are very much slower than the rates of formation. This is a justifisble approximation, since we cbserve that a one second exposure to the exciting light produces cation and electron pairs that require two to three hours to reconbine. The particular solution we present here requires weak absorption - which we can control by concentrations, and ideally narrow wavelength band absorptions, arrow band absorptions were not possible, so that extinction

coefficients referred to are the average over the absorption bands.

?The solution is

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=e

Io? fee'yA a ne

I*beva

Z refers to the total number of ionization events produced during the excitation period AT , Io is the incident exciting light intensity; ¢, and ?' refer to the extinction coefficients of the neutral and triplet state respectively, d the optical path length; i.e. 1 cm, and ?Tis the natural lifetime-of the triplet or = ibe +5). Thus, the relationship requires that Io°/$ have a linear dependence on the exciting Light intensity.

We take the value of the quantity J, to be proportional to either the total amount of prolonged luminescence, the total emount of infrared stimilated luminescence, or the total anount of thermoluminescence, Tais quantity, measured Coulonbs of photamltiplier current, is plotted in Figures 12 end 13, according to the above expression and the data is obtained from the three forms of reconbination lunimescence. The ratio Ig/z 4s linear with Ig , but is plotted on a senilog scale for convenience,

The data referred to as electrical integration vas an attempt to accumulate the photamltiplier current on a capacitor, in contrast to a manual method of integrating the photomultiplier current vs. time ~fron a strip chart recordings - by a graphical method. the TZ acquired in this fashion is very much lower than from the other methods, This 48 not to be taken

evidence that considerably less recambination occurs

uring warming but rather that the capacitor used in the measurenent

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ost @ considerable fraction of its accumiated charge through Lesage during the course of the experiment. Comparative data for the Z obtainea during warming showed that the electrical method gave data lover by two orders of magnitude than the manual integration method. In Figure 12, ?the isothermal and infrared stimulation data were performed with a concentration of 2 x 104 aniline, while the thermoluninescencent date, for aniline vere obtained with a concentration of the order 10°74, the data presented in Figure 15 vere obtained with an indole concentration of 5x 107M.

The existence of the Debye-Eéwards intensity dependence, the effects of infrared stimulation, and the thernoluninescence indicate the occurrence of photoionization anong these compounds. The existence of @ squared intensity dependence in egreenent with a biphotonic mechanism involving the triplet state, indicates the path by which photofonization has occurred in the cases of indole, indazole and aniline. The occurrence of biphotonic photoionization in aniline

has been observed previously.2 as

Section B: Theoretical work

?The theoretical work has continued along the basic lines indicated previously. One objective of this part of the program is the calculation of excitation energies of radical anions and cations of heterocyclic molecules, to aid the assignment of experimental spectra. The other objectives include the general features of the electronic structure of such species, and work has also been begun on electron-nolecule inter-

actions.

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T. Electronic spectra of Heterocyclic Radical Cations and Antong

The results which have been obtained for the doublet-doubret transitions of the radical anions of pyridine, pyrimidine, pyrazine and pyridazine are fully described in the appended article, vnich nas been submitted for publication, These calculations use the Pariser. Parr-Pople self-consistent field method, with and without Configuration Interaction. The results can be summarized by saying that an excellent agreenent was obtained with experimental and theoretical results of other groups of workers: as ve11 as with the experimental vork reported earlier. The use of limited Configuration Interaction does not improve the agreenent with experiment, in harmony with recent theories.

In edition to the above calculations, the radical cations of the following molecules vere examined: pyrrole, furan, thiophene, Pyridine, pyrimidine, pyrazine, and pyridazine. A very much poorer agreenent with experiment 1s obtained for the radical cations.

?The Pariser-Parr-Pople method uses the pi-electron approximation, #0 that these results question its validity for such radical cations. For the anions the unpaired electron is certainly in an antibonding pl-orbitel, and the approxination appears to give good results. However, for the radical cations of heterocyclic molecules, it is by no means certain whether an electron has been renoved fron a signa (non-bonding) or from pi-orbital. Pyrrole ie the only cation whieh hhas been examined which has no non-bonding electrons available, but

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the results for the ryrrole cation are equally bad. This indict

that as well. as taking account of the signa-electrons, it may be necessary

to specifically include the signa-pi interaction terms. ?These give rise

to a reorgenization in the signa-franevork on ionization of a pi-electron,

which will significantly affect the stability of the rafical cation,23-25

?Mis point is currently being investigated. No method exists at present,

apart fron al initio calculations, which includes this type of interaction.

II, Velence-Bond Calculations on Heterocyclic Systens

These calculations use cyclopentadiene as @ preliminary model, and ain at the electronic structure of simple heterocyclic molecules and radicals, using non-empirical valence bond method, as described in previous Reports. During this year, work has been principally on the modification of a program originally written by Dr. Palmieri (University of Bologna). This uses as input the atanic integrals whose calculation was described in Technical Progress Report No. 3 (PRNC-116). All possible determinantal basis functions of a given multiplicity are generated,

and the integrals among then evaluated using Lowdin's density matrix

formation for non-orthogonal Slater determinants.

III. Hetaryne Intemediates

In collaboration with Dr. W. Adam (U, of Puerto Rico) and

Dr. R. Hoffmann (Cornell U.) a study has been completed of the 'hetaryne

intermediates' formed by removal of hydrogen atom(s) from heterocyclic

molecules. This work has been accepted for publication, and a copy

4s appended to this Report. ?The electronic structure of these

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intermediates was examined by the Extended Huckel Theory, 6

which
includes signa- and pi-valence electrons, The trends in stability
correlate very vel with experimental data, and were analyzed in terns

of orbital splitting patterns.

IV, Electron-Holecule Interactions

Work is beginning on the calculation of exact molecular potentials
between an electron and a many-electron molecule, in the form of a mlti-
pole expansion.?? this potential is to be used in investigations of

electron-molecule attachnent processes.

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COMPOUNDS IRRADIATED ATTPX.GIVING ERMOWINESCNE

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SR OF GAMMA = IRRADIATED CYTOSINE

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Figure 1 ?aerimtive ctr

ESR OF GAMMA IRRADIATED URACIL

Figure 2

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TABLE 2

INSTRUMENT DESCRIPTION FOR FIGURES 3, 4AND 5

A. General Electric AH6 high pressure mercury arc

B. Arc power supply

C. Ni-Co solution filter

D. Baird Atomic interference filter 254 nm

E. Slit

F, Photographic shutter

G. Dewar box

H. Quartz dewar

|. lem quart solution cell

J. Stroboslave 1539A flash lamp

K. Flash power supply and trigger unit

L. Bausch & Lomb 603AB high intensity grating monochromator

M. Wavelength drive unit

N. Emi 9526B photomultiplier

0. Fluke 4128 high voltage power supply

P. Keithley 610B electrometer

Q. Leeds & Northrup 10 mV recorder

R. Tektronix 561A oscilloscope

S. RG-1000 Jena filter

T. Boxter Corp. 5900 variable intensity tungsten lamp

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APPENDIX 1.

Submitted to the Journal of Physical Chenistry, Janurary, 1969

BY PYRIDINE AND THE DIAZINES IN y-RADIOLYSIS:

?THEORETICAL COISIDERATIONS*

?A. Grinison, G.A. Sixpson, M. Trujillo Sénchez, and J, Jhavers

Puerto Rico Hwclear Center, ** and Departments of Chenistry and

Physics, University of Ruerto Rico, Sen Juan, PsR., 00935

Avstract:- Absorption spectra characterizing the radical anions of pyridine, pyrinidine, pyrezine end pyridazine have beon produced by 7-radiolysis of the parent compounds in a Reniethyl-tetrezydrofuran matrix et 77°K. These spectra are in good agreenent with those obtained by chemical reduction or electrolysis, but some additional transitions at longer vave~ Renths have been observed. Pariser-Perr-Pople calculations of ?the theoretical doublet-doublet trensitions of the radical anions yield good correlations with the experimental transitions. ?The best correlation is obtained by not including configuration interaction, at least for e very limited mmber of configurations. Irradiation of pyridine in 3-nethylpentane leads to & themdluninescence assigned to the phosphorescence of pyridine.

?Fresented in part et the Second Tnterascriean Radiochonia Conference, Hexico City, Mexico, April 1958.

**Puerto Rico Nuclear Center is operated by the University of Puerto Rico for the U.S. Ateate Energy Comission under Contract AT(H0-1)-1833.

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Our prinary interest?in the production and characterization op

Sonic intermediates formed by the y-rediolysis of heterocyclic rotecures,

This identificetion can provide important information on the effects of

radiation on biological systens, The technique being used 4s that of

Asolation in a solid natrix et Liquid nitrogen temperature.) Fron the

es

2) A.M. Bass end H, P, Broide, "Formation and Trapping of Free Radicals",

Acedemic Pressy New York (1960).

chemical viewpoint, perhaps the most intruiging aspect of such vork is

the extreme simplicity of the final processes forming these intermediates,

?Thus the work of Hamil) end co-workers? has indicated how radical anions

29M. Re Ronayne

~» Je P. Guarino end W, H. Hamill, J. Am. Chem, Socey

Bi,N25O (1962

can be formed by attachnent of low energy electrons to solute molecules.

Radical cations can apparently be produced by a simple positive charge

exchange between the matrix and the solute nolecute,2+4 In a previous

?SSSSSSSSS???

3 T. Shida and

2 2 He Homild, J. Chem. Phys. bh,

2369 (1955).

A. Grinison and G. As Sinfoon, Je Baye, Guat, oo UIE (A568)

ee EEE

publication," ve have described one radiolytic technique suitable fo"

the production and stabilization of radical cations, By this meansy

absorption maxina measured et 77°K Were assigned to the radical caticr®

of pyridine, pyrrole, and thiophene. rn general, the production of radical anion intemuediates 4s experinentelly much less difficult. TH

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Hush and Hopton have reported the ebsorption spectra of the radical entons of pyridine, ryrazine, pyrinidine, and pyridazine, produced by reduction with sodiun metal in tetretydrofuren at room temperature.5?6 Kinnel. end Strouse? reported the optical spectra of the some radical enions, produced by electrolysis in liquid amonia solutions, ?The observation of a Xnax at 330 m from alkeli metal solutions in anhydrous pyridine at roca temperature

5) 3. W. Dood, Fs J. Hopton, and W. 8. Hush, Proc, Chem, Soc. (Tondon) 61 (1962).

6) F. J. Hopton, Pa.D, Thesis, University of Bristol, England (1952),

3 P, I, Kinnel and i. L. Strauss, Abstract of Papers, Anericen Chenical Sockety Meeting, San Francisco, March 31 to April 5, 1958, 8-251-, and private communication from H, L. Strauss.

4s in good egreenent with the earlier reports for the pyridine anion.®

8) C, D, Sctmlbach, C, C, Hinckley, and D, Wasmund, J. An. Chem, Soc.

90, 6600 (1958).

The present paper describes our results on the effects of 7-irrediation

on the optical spectra of pyridine end the diazines in organic glasses

at TI°K. the major process observed under these conditions is sho to

be the attachnent of an electron to the neutral ezine molecule to for

the radical anion, The experinentelly observed optical transitions froa

the different experimented techniques are show to be in excellent accord.

Finally, the seni-cnpiricel theoretical excitation energies for the

redical anions, calculated by us, by Hush and Hopton,© end by Kimsel and

Strauss! as compared with the experimental velucs.

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ental Techniques

Pyridine, Eastman Spectrograde, vas distilled from bariua oxide before use in absorption spectra detemsination. For emission studies Fyridine solutions were prepared either froa the distilled pyridine or fron a middle fraction of the main peak of samples injected ona 6 ft, GIC column of Carbowex ooh 80°C.Good separation of pyridine and its ?Juminescent impurity, pyrazine uy were achieved under these conditions,

ee

9) C.J, Breadey, J, Chem, Pays. 2h, 572 (2955).

Se

Pyrazine, pyridazine, and pyrimidine were best comercial grade, end were used without further purificetion, 2-Methyltetrahydrofuren (MTHF) was purified by pascage over alunina, and stored under vacuun in a storage vessel containing Na-K alloy. 3-Methylpentane (MP) , Phillips Research Grade, was passed over a silea gel colunn, then stored under vacuum over Na-K alloy. Solutions of required concentrations were prepared fron these purified solvents on the vacuum line by standard techniques. y-Irradiations were perfomed in the FRIC 2700 curie 60-60 source, using the Fricke technique for dosinetry.

Avsorption spectra vere obtained vith the eyparatus and techniques desorived previously. Optical bleaching was effected with a 250 watt quartz-fodine Lanp and appropriate transnission filters, Enission spectra under thermal stimulation were obtained efther with an Aninco-Bownan spectrophotofluorineter operated with @ 100 na band pass and a 1728 photomiltiplier, or a motor driven Bausch and Loub " High Intensity " monochrenator (No, 33-06-25) at 50 mm band pass end an EMT 95263 photomltiplier. The somple cell end optical devar vere namtttea

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to warm up in the spectrophotofluorineter by renoving the Liquid nitrogen, Enlesion spectra were then obtained by repeated scanning of the spectra at @ rate of one scan (200-700) per minute, The heating rate under these conditions ie Linear during the first five minutes, at epproxinately 20°K/ninute,

THROKBTICAL CALCULATIONS

?Theoretical excitation energies and oscillator strengths corresponding to doublet-doublet electronic transitions in the azine anfoné have been carried out using the sent-enpirical Pariser-Parr-Pople (PPP)

self-consistent field technique.? Recent non-empirical calculations

on the excited states of the ethylene molecule? including OT interac

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20) R. G. Parr, "The Quantum Theory of Molecular Electronic Structure", W. Benjenin, N.Y. 1953.

2a) 8. H, Dunning end V. Mekey, J. Chen. Phys.) 47, 1755 (1967).

tion have given e sorely-needed Justification for the reduction of the

Pi-electron integrals in the PPP method below the theoretical values.

This can be considered as taking account of the effect of screening of

?the TT -electron repulsions by the T -electron distribution, In

heterocyclic molecules, there is no reason to expect the sinilarity

between radical anton and radical cation spectra suggested for the

@lternate hydrocarbon systens.1? In particular, in calculeting the

eee

22) H. C. Longuet-Higgins and J.A, Pople, Proc. Phys. Soc. (Lenton),

468, 591 (1955).

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electronic properties of the azine radical cations, some thought must 4_

given as to whether the missing electron has been removed from a lone

Pair orbital, or fron e pi-orbital. However, for the radical entons,

the additional electron enters a pi-antibonding orbital, so that the use

of e pi-electron calculation in predicting electronic excitations is

Sustitiea,

Input wavefunctions for the PPP calculation were obtained trea Huckel calculations on the appropriate neutral heterocyclic molecule, using conventional parameter values. As a variant on this approach in Sone preliminary calculations, wavefunctions from a 10-iteration W-

technique cateulation? on the actuel radical antons vere used es input to the PEP program. However,

?the comparative "veakness" of the W-

technique in making electron density corrections to the coulomb integrals ?was shown up imediately, Thus, after one iteration of the PPP caleula- Adentical results obtained trom Huckel and @-input wavefunctions: Te Pareneter values which vere use,

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15) A, Streitvetser, "Molecular Orbital The

ory for Organic Chenists",
John Wiley end Sons, Inc., WY. 1961, pod °

Pp. 115,

ere Listed in Tebie 1,

tion,

4 in the PPP calculations

A

Matted contiguration interaction (CI) ¥8s

?the groun:

Ground state end'5 excited doublet states

The diagonal and oft-as,

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Pf

the relatively limited configuration interaction,? it ds not suxpricing

2s) N. L. Allinger ena 7, W, Stuart, J. Chom. Fhys., 47, W611 (1957).

that CI actuelly coused a slight deterioration of the egreenent between theory end experiment, The CI velues are therefore not reported in this paper.

RESULTS AND DISCUSSTON

PRDDE

The spectrum shown in Figure 1 illustrates the absorption bands Produced on radiolysis of MTHF solutions of pyridine. The 1200 nn bend corresponds to the position of the trapped electron band in pure MINP, ?The band et 340 nn is cheracteristic of pyridine in MiP, Liberation of electrons by photolysis into the trapped electron band is expected to increase authentic radical anion absorption bands, as the liberated electrons are cepturalby unreacted neutral solute molecules.? mleaching the trapped electron band in irradiated pyridine-HTHP solutions causes an increase in the band near 340 m, as shown in Figure.1, Addition of 2 x 10° trifiuorocthanol, an electron scavenger, to the pyridine-i solution prior to drreaiation results in the non-appearance of the 340 nm band, Figure 2 shove the depentence of the absorption at 340 rm end at 1200 rm on the initial pyridine concentra ton, The net sbsorption at 1200 m falis off very sharply with dnereasing pyridine concentration, reaching a limiting (but non-zero) value at ebout 1x 107M pyridine, this suggests that the efficiency of ryridine for eaupeting for electrons against solvent treps ie fetrly high, simltaneously the 340 mm ebsorption decreases, but reaches e limiting

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Value at a greater pyridine concentration, This is due to a decrease in the underlying trepped electron and associated methyltetrehydrofureny radical} absorptions in the 340 nm region, counteracted by a build-up

?_?_??

ee

in the pyridine 540 na ebsorption, At concentrations greater than

4 x 20°, a component of the absorption can also be observed with a maximum at 500 no, Only in the concentration region 8 x 10> to

4 x 10°? does bieaching the trapped electron band result in an increase 4n the 340 nm bana,

The fact that the 340 nm band can be increased on bleaching the trapped electron band, and is decreased on addition of an electron Scavenger, denonstrates the presence of an anionic intemediate of Pyridine, This is believed to be the pyridine radical anion, fomed by the attachment of an electron to pyridine, The assignnent of the 340 nm band to the pyridine radical anion is supported by @ number of

15) F.S, Dainton, and G. A. Salmon, Proc. Soc., London A. 285, 319 (965).

independent observations, iscussea below. However, the fact that an increase in the 310 nu absorption following trapped electron bleaching does not occur et high pyridine concentrations requires sone aiscussions One explanation 8 to assume a weak optical transition of the pyridine enion at wavelengths greater than 1000 ma, which can give rise to a Photo-ejection process, Thus, the bleaching process at pyridine con

centrations greater than 4 x 207% vould cause tvo ecapeting processesy

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capture of electrons released from matrix traps, and photo-ejection froa pyridine anions, Where there is a lov trapped electron yiela,

?the photo-ejection process dominates the capture of trapped electrons released by photostimilation, and a decrease in the 340 nn absorption results, Supporting evidence for the existence of a long wavelength transition of the pyridine enion may be teken from the eppearence of the Limiting concentration yields of the trapped electron band in Figure 2, The non-zero value of the ebsorption suggests that the extinction co-efficient of the pyridine enion at 1200 nm may be as high as 204 of the value at 340 no,

To confirma the assignnent made in MTHF, and to investigate Possible enission froa irradiated somples, a series of studies were made in a 3-nethylpentane (uP) matrix at 77°K. The advantagesin using this matrix are that the trepped electron band occurs at a longer wavelength

17,18

(2,700'na), and that recombination luninescence has been observed.

36) D, W, Skelly and W. H, Hanill, J, Chem, Phys., 43, 3497 (1965), and

W. Hy Hani, private comunteation,

1]) A, Dérouléde end F, Kieffer, Nature 215, 1475 (1967).

1} Se Gperey a. ante: Dees eee cease, send

Acad, Sci, Paris, 264, 1013 (1957).

Figure 3 shows the absorption spectrun at 77°K following radiolysis of pyridine in MP glass. In addition to the trapped electron band, absorption maxina ere ebserved near 1200 rm and at 360 ma, with an inflection near 500 ma, ALL of these bends aisappear on varming the ecxple, If the sample is allowed to decay isothemally in the dark for 8 hours, the trepped electron band is reduced to less then 104 of the origin)

vatue 2?

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19) J. B. Galliven end W. H. Hamill, J. Chen. Phys. Wh, 1279 (1966),

Simultaneously the bends at 1200 and 360 nm become more pronounced, as shown in Figure 3, The absorption at 1200 m after decay, which are clearly in excess of 104 of the original absorptions, confirm the existence of a long wavelength transition of e pyridine intermediate, suggested earlier, The failure of the 350 ma band to increase after escape of trapped electrons suggests the presence of an additional Intermediate which acts as en electron scevenger in the MP matrix, Sone preliminary luminescence observations of the pyridine MP system may be reported here since they ere pertinent to the discussion of pyridine intermediates and are novel in their significance, On warning solutions of irradiated pyridine-MP glasses luminescences vere

observed, In addition to the solvent emission band at 425 nm, 9

20) M. Burton, M, Dillon, and R. Rein, J. Chem, Phys. 41, 2228 (1951).

structureless emission band at 355 + 10 nn was observed, lasting up

to 10 minutes after renoval of the liguid nitrogen, This emission

band was ebsent in pure MP glasses. Use of GIC purified pyridine gave

?the sane result. ?The warm up luminescence obteined from an irradiated

MP glass containing pyrazine, the usinescent impurity in pyridine,?

had a maximum at 38045 mm. Phosphoresce of pyrazine occurs neat

380 m.21 therefore, the enission observed with pyridine-MP glasses

21) L, M. Logan end I, G, Ross, J. Chem. Phys. 43, 2903 (1955).

iain

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is associated only vith pyridine and not a contarination. ?The veven

Jength corresponding to the maximum of pyridine phosphorescence can be estimated fron the oxygen perturbed singlet-triplet absorption spectra[22] to be greater than or equal to 337 m."" Thus, the emission may be due to pyridine phosphorescence following reconbination reactions. The Airect phosphorescence of pyridine via intersysten crossing fron an excited singlet state hes apparently not been reported yet. The above interpretation requires the presence of the pyridine cation ratical, Which we have reported previously" to have @ dowx at solely 380 na, The observed bana at 360 mm may thus contain unresolved components of doth the enfon redical (340 mn) and cation redical (380 mm) absorptions. The formation of both entonte and cationic intermediates in MP hes been suggested by other workers.25 he decrease in the 360 band on decay of the trapped electron band would then be attributable to the aisep-pearance of the cation conponent, The long lifetine of the observed enission band suggests that, in addition to electron-cation recoabination, Phosphoresconce can be produced by enfon-cation recosbination processes at higher tenperatures,

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22) D. F. Evans, J. Chem. Soc., 3385 (1957).

Teble 2 gives @ sumary of the transitions attributed to the Byridine redical enion in this vork, and the experimental assignments

5,6

of Hush and Hopton,??? and Kimmel and Strauss.? the egreenent on the

Position of the near uv bend is excelent, considering the very different

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?xperimental techniques. ?Thus Hush and Hopton's (HH) results refer to Solution in tetrahydrofuran at room temperature, and Kimmel and Strauss (x8) resutts refer to Miguta emonta solutions. ?These other workers Observe additions shorter wavelength transitions which cannot be verifies under our experinentel procedure, The theoretically predicted doublet. doublet transitions of the pyridine radical enfon are collected on the right of Teble 2, Our results, which do not include CI, give high oscillator strengths as expected, but ere otherwise in better accord with the experimental results, ?The band at 3.7 ev is calculated at 4.29 ev, whereas KS results give 3.07 ev, end HH have no corresponding band. The band observed by HH at 5.08 ev and by KS at 4.75 ev is calowlated by Hit at 5.25 (allowed band) ev, by YS at 5.26 ev, and by us at 5.40 ev Tae suspected band at 2.5 ev (500 mm) corresponds to a predicted pyridine anion absorption at 2.66 ev (il) or at 2.25 ev (this work). Pinelly, our calculations alone suggest a forbidden long wavelength transition.

By using the extinction coefficient of HH for the 3.37 ev band, we

estimate a G velue of 2.7 for the production of the pyridine anton at

high pyridine concentrations,

?PYRAZINE:

Figure 4 shows the absorption spectrun at 77° after y-radiclysis

of Fyrezine in @ MTP glass, and the result of bleaching the trepped

etectron bend, An absorption maximm is produced near 345 mm, and ine

suitable concentration region, an increase in this absorption is produced

by bleaching the treppea electron band. The concentration dependence of

?Shese bands have not seen studied extensively, but it has been coserved

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=

that the position of the Amex increases vith increasing initia

concentration of pyrazine at constant dose. specifically, @ rnex

of 320 m is found at a concentration of 1 x 107, which incresses monotonically with concentration to a max of 345 mm at a concentration of kx 10%, We attribute this effect to en artifect of the technique of determining spectra, Difference spectre ere obtained by substracting the initial gless spectrum fron that after irre- @lation, This essunes no decrease in the near uv bands of the parent heterocyclic during radiolysis. Pyrazine has been found to have a Amex of 315 ma in MTP, in comparison with the value of

6,23

328 m in cyclohexane, ?This marked blue shift characterizes

the n-

* nature of the transition,

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25) M. Kasha, ?A Symposium on Light and Life", Johns Hopkins Univ. Press, Baltinore, 1961, p. 31.

?Thus, depletion of pyrazine at lov initial concentrations can cause shift in the apparent position of the nearby absorption of ?the pyrazine intermediete, This was denonstrated further by repeated irradiation of the sane solution to successively higher doses. On obtaining difference spectre in the usual manner, @ shift in the

dmax to shorter vavelengths with increasing dose was observed. The Position of the near uy band of the radiation induced intermediate

of pyrazine is thus assigned to be equal to or greater than that observed at the highest concentration studied. As e result of the

sbove observations, an ebsorption maximum at 345 nm 4s assigned to

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- hee

Sr anionic intemediate of pyrazine, This is believed to be the Praing Fedieel anion, formed by electron attachnent to Fyrazine. The generat features of the concentration dependence of the spectra show qualitative Sinilarities to that observed for pyridine, At high concentration (7 10°71) « maximum is resoived at $00 m, Also at these concentra tions the 340 band decreases on bleaching the trapped electron bana, This suggests the existence of an unchserved long wavelength transition of the pyrazine enion, Teble 3 compares the ebove assignuent for the pyrazine redical anion with the results of 12° ena x5.? Again there 4s substentian accord among the three groups of investigators for the near uv bend, renenbering that our experimental value represents en upper linit to the transition energy. Again the theoretical excitation energies Provide a reasonable account of the observed transitions, All three calculations give excellent accord with the high energy transition near 5 eV. For the band near 3.5 eV, KS (3.15) are in good agreenent, vhereas our value of 1,70 eV is very high, and that of Hi ds very lov (2.90 ev), This letter value may be related to the suggested 2.45 eV (500 nm) band, for which we calculate 2.28 eV. A forbidden long waver Jength transition is predicted near 0.5 eV, By using the extinction coefficient of Hii for the near uv bend, we estimate a G value of 1.7

for the production of the pyrazine enion at high pyrazine concentrations

PRDGDE

Figure 5 illustrates the ebsorption bands produced by raticlysis

of pyrimidine in MTHF at 7°K, and the result of leaching the treyped

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hg

electron band. An absorption maximun is produced near 320 nm, which is increased by bleaching the trapped electron band for a suiteble initial pyrimidine concentration, As for pyrazine, a shift was observed in the position of the Xmex with increasing initiel pyrimidine concentration at constant dose, This effect is again attributed to depletion of the underdying neutrel yyrinidine sbsorption, The band 4s assigned a Anax of 320 nm, in MTF at 77°K, For concentrations above 2x10 M, # further ebsorption. band can be resolved near #00 nm,

Table 4 compares our results for the pyrimidine radical anion with those of Hf? ant 13,? Again our exporinentel transition energy for the near uv band is very slightly higher than the values of these other workers, for the reeson explained earlier, Our theoretical calculation gives @ predicted band at 4.04 eV, in better accord with the experimental value of about 3.8 eV than the result of Hi (2.8 eV) or of KS (3.01 ev). For the band near 5 eV, the values of HH (5.09 or 5.47 eV), those of Ks (5.36) and our value of 41.73 or 4.94 eV are ell in reasonable accord with experiment, In edition, the exist, ence of e transition near 3 eV (400 nn) reportea by us is supported by calculated transitions at 2,86 eV (#i),3.02 ev (ks , but may refer to the 3.8 eV band), end at 2.53 ev (?thle work). A virtually forbidden long wavelength transition 4s egain Predicted, Using the extinction coefficient of Hit for the near uv bent, we estinate a G value for the production of the pyrimidine anion of 2.1 at high pyrimidine concentrations,

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PRDZDS

Figure 6 sho:s

Pyridazine in y

ebsorption bends profuced by ratiery

et T7°K and the result of bleaching the tr:

Stectron band, fin sbsorption band {s produced with dex at 35):

intensity is increased on bleaching the trapped electron bent,

radical enion, Figure 6 also shovs ot?

et 900 ma, end betueen KOO end 700 my

?The data in Teble 5 indicate the excellent egrees

hear uv band of the pyridazine radical anion enong the different

Groups, Our theoretical excitation energy of 4,54 eV does not e:

very well with the experinentel value of 3.5 - 3.6 eV. The value of

XS (3.20 eV) is setisfectory, but Hi heve no closely corresp

nBing

and, The bend found by Hi at 5.13 e¥ is satisfactorily eccomted f in ell three calculation

In edition, the possible existence of be:

?at 2-3 ev (4100-700 rm) end et 1.75 eV is partly supported ty &

calculated bard et 2.73 eV (ii) end at 2.15 eV (this work). Using

the extinction coefficient of Ei for the near uy bend, we est!

8G velue of 0,8 for the production of the pyridezine reiical ante:

caucLuston

The results of these investigations, texen jointly with th?

measurenent of ?authentic! redical enion spectra by tro other Erour®

of workers, denonstrate the forzation of the ezine radical enters {2

yoradiolysis et T7°K by the electron ettactment process

Azine +e? ?> (Azine)?.

ectra of the four ezine radical e4

The experizentel ebsorption

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= us.

are therefore feirly well established, the reasonable eecord between

?the experimental transitions and the theoretical transitions, in the

f-electron approximation, confims that the additional electron enters

a 7 * antibonding level. In the present calculations, no direct

account was taken of the T-reorganization expected as a remit of

this additional electron, We feel that specific inclusion of this

effect would provide e more adequate account of the electronic structure

of the radical enions, end are currently investigating this possibility,

The present thermoluminescence results suggest a pyridine phosphorescence

near 305 mn, If this essigment proves correct, then a fruitful eres

of spectroscopic investigation wil becone possible. Since many

compounds have little or no phosphorescence, such as pyridine due to its

negligible intersystem crossing efficiency,?# production of triplets

2h) J. Lemaire, J. Phys. Chem. 71, 612 (1957).

??

via fon reconbination may well provide the only method of characterizing the phosphorescence, Extensive work is in progress not only to substentate the pyridine emission, but also the themoluninescence fron other non-phosphorescent conpounds.

ACKIOLEDGRENTS

this work ves supported by a research graitfren the Division of Biology end Nedicine of the U.S. Atoute Energy Comission, We also wish to ecknowledge the Kindness of Professor Hush end Professor Strais in communicating unpublished results, to thank Professer Hontil for hele ?ful. discussions.

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?TABLE 2

PARAMETER VALUES Ii! PARISER-PARR-POPLE CALCULATIONS

Motecule

Pyridine, Pyridine

Radical Anion

Fyrezine, Pyrazine

Radical Anion

Pyrinidine, Fyrintaine

Radical Anton

Pyridezine, Pyridezine

Radical Anion

Coulonb and Resonance

Ky = -h5,865

Hoge Hog = ?¥2.535

ig, Hog = -h2.374

iy, = -k2.303

Hy = -2.62

Tigg = -2.29

Hygy * ~52.502

Hoar Haz» Hess

2 gg? ?6

Hoy = 2.62

Yop * 2.29

Hygit ~50.736

Byp © -t2.862

Hy > Hyg = 2.610

Hy, = -H2.550

Roy = -2.62

gg = -2.29

Figg = 048.755

Hopp Hg = -he.595

Byyy gg * -42.to3

Bygy © -2.25

Roy, © -2462

Bigg = -2.29

Repulsion Integrals (ev)

a) = 32.310

fe), (jee) TIO

ae y eg) * = 5.608

22/38), 03 CH), (04/5),

?ul), 1»

(ev de efi (33/55),

(22/55), (33/66) = 4.950

(Qiai/iai) = 12.340

fes/e2) = 11,230

za), (11/66), (5/88),

On), On/5) (al,

22/55) = 540:

(22/66), (33/55) = 5. 3°

ray/iat) = 22,340

lecfoc) = 11.330

?Gal, (22/68), (22/53),

= 75776

5 2 4.989

3/55), (33)

af 4 eres, ?diy = 54560

22/55)

1/55), (65/68) = 1.555,

ae Bi =e en

55,

By, fe

1

fe (44765)

= 950

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=u.

TAB 2

TRANSITION ENERGIES (eV) FOR THE PYRIDINE ANION

Experimental values Calculates values

a7 This work 6 Rett This wort

wk 026.000,

25 266 Loon 2wioy

370m) 3.46LoM) 3. 30700) 4294195

46.0

ania 5.05 coon 50.17

5.08 20) 5 B80 5.25.00

(scllator strength values in parenthesis.

TABLES

TRANSITION ENERGIES @V) FOR THE PYRAZINE ANION

Exgerinenta

Cateuites values

fag RET

6 RT

290.068

3acoa 3580m 3 315 055

anisa

56.29

496029 5.211) 52m 3s4L2e

Oscillator strength values in parenthesis.

TABLE 4

TRANSITION ENERGIES (eV) FOR THE PYRIMIDINE ANION

imental values atelated valves

TT sere Re6 RT This work

29.003)

a 2.85 com 253085

315LOM = -ATL06) 89 ROL) ? 4084710

asrase 51429 5.0L 5.3601) ATL

5.47 C060 a mciR

Oscillator strength values in parenthesis,

---Page Break---

TABLE 5

TRANSITION ENERGIES (eV) FOR THE PYRIDAZINE ANION

Experimental values Calculated values

Ref. 6 Ri This work Ref. 6 Ref. 7 This work

LIS 0.27 (000,

23 2.73 .05)) 213.6169)

3.521.052) 3.64 (065) 35 3.20 032) 4,54 (185)

4.59 (030) 4B 1.235)

5.13 (182) 5.24062) 5, 63 (125) 5.27 (210)

Oscillator strength values in parenthesis.

oo. scorpion spectrin of an rvttte aeation of Pyridine,

id 830° fa ne.

attr tne ot 6 eof,

LA er 5 eines Bet b= 690 mm

(Coming no, 652.64 fiser)

os

4

L

Toso T2060 1300 am

Figure 1

---Page Break---

ah e

Region where uv

0-0] band increases on

ir bleaching

Les

Figure 2

Concentration depentence of sbeorption bands produced

on radiolysis of Fyridine in TIP «

° dose = 2.9 x 20 ov/t

© opticar density at 30 ma,

os

4 optteat density at 1200 a,

00,

Figure 3

of rine ho x 20%

steer toe of 228 0? t/t,

---Page Break---

on,

20] serpice spectrin of orale pttient

?of Pyrazine, 2.0 x 10°%H sn Mere.

ts ater tne ce 12 rf

er 15 mins each 972000 m,

12] (estets no-texo fuer)

2

4

L L 1 1 L L

700 300 305 7500 20d 400 am

Figure 4

00,

1

?Aosorptien spectra of an teretinted solution of

Pyrtnttine, 5.2 5 74 So He,

etter aone of 3.8 3 ef

stter 2 ute Beach, 29 1000 mm,

(eanote roaoio einter)

300

Figure 5

---Page Break---

- ol

senate of ridacne, 045 WA

etter one of 1.2 0 20 ef

ster 3 minste watateres exposure

x to Quarts Katine emp.

L

380" 560.400 605

Figure 6

---Page Break---

---Page Break---

APPENDIX 2

Accepted for publication by the Journal of the

?American Chenical Society

HETARYNE INTERMEDIATES

Woldemor Mum, Alec Gritison, ond Roald Hoffmann? (Department of Chemistry

2

cond Puerto Rico Nuclear Center, University of Puerto Rico, Rio Picdias, P.Rey

00931, and Depariment of Chemistry, Comell University, haca, N. Y., 14250).

ABSTRACT:

?The electronic structures of all of the posstble 1, 2, 1,3, and I, =

aromatic intermediates derived from pyridine and the diezines (boteryns

cs) have been calculated using the extended Hickel theory (HT)

opytidines, itis found thet of the six possible isomers, the 34

at stable, and the 2, 6-didshydropyridine the least

Iso predicted for 4,5-didehydropyrozine «nd

nal rnd in the hotnyne

For the

didchydropyti

stable. Great relative stobi

4, 6-didehycropyrimidine, The complex co

stobilities eon be rationali

ofthe enol Inforactions entong nexr-bening redfea lb tic

orbitals, A dominant effect is shown fo be a nitrogen lone p:

of neciby redical lobes. The ealeulated stability sequences and total election

tal data

distributions provide an excellent conelation ef the eveileble experinel

ity ond orfentation effects in the hetoryne intemediates,

---Page Break---

= 5h

The chemistry of dehydroaromatte intermediates derived from heterocyclic

molecules has been actively investigated during the lost decade. Numerous popers

have been published on this subject, together with extensive reviews by den Heriog

and van dor Plas®, by Kauffmann, and by Hoffmann®. Prinetpal attention hos

been focussed on the I, 2-dehydroaromatics derived from nitrogen heterocyclies

ine, quincline, isoquinoline, and the various diozines. These inter

such os pyri

mediates are usvally formed by the dehydrohalogenation of the corresponding halo=
genated heterocycle on treatment with @ strong base. The two adjacent radical ~
lobes in the 1,2 intermediates are thought to overlap appreciably, forming @ par
tial triple bond in the heterocyclic ring. These species have been designated os

ty exists, in principle, of forming 1, 3- and 1,4~ dehydro=

hetarynes. The possi

aromatics, in which the radical lobes are respectively in meta~ and para~

tions. However, no such intermediates eppear to have been reported to date.

The only member of the 1, 3-sories that has received some attention is 2,6?

6

Here it has been postulated that conjugation through the

dehydropyridine

nitrogen lone pait,. which is flanked by the two radical lobes, should provide

the necessary stabilization for the formation of such an intennediate.

In comparison to the dehydrobenzenes, the hetarynes are considerably more

?complex. While benzene can only form one 1,2~ dehydro intermediate, pyridine

can form either 2, 3-dehydropyridine or 3,4-dehydropyridine. OF these two pos sible hetorynes, 3, 4-dehydropyridine is formed preferentially in the dehydrohalogenation of 3-halopytidine.? It has only been posible te prepare 2,3-

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dehydropyrdine by blocking the 4-position by wbstittion.® While the synmetse dchydrobenzene intermediate gives a single product on reaction with a nucleo

phile, the unsymmetric 3, 4~dehydropyridine can form two products, by substitution

?ot either the 3-position or the 4-position. The preferential atteck at the A-posttion in 3, 4-dehydropyridine provides some evidence for an importent orientation tfect > Very little theoretical work seoms to be evatlable on these intresting hetanyne intermediotes.® For this reason, we decided to examine @ number of

dehydroheteroaromatic molecules, using all-valence electron calculations of the

extended Huckel type (CHT)?

THEORETICAL ANALYSIS

Extended Hickel calculations? on the six possible didehydropyridines result

in the following stability onder.

Oo O

500.23 oV -499.74 oV -499.69 oV

A B c

499.41 oV 499.51 0V 496,53 oV

o E F

---Page Break---

- 56 =

; Ih conticat to-a previous simple Hickel ecleuly.

fon, which indicated the 2, 3-dehydropyri

(0) es the most stoblo®, the 9,4.

dehydropyridine (A) clearly emerges os the most stable isomer. ?The 2, Sedshydio

isomer in fact is so dest

ized that it eppears in our calculations with o hig

energy thon some meto~ and parchetarynes.

This agreement with one of the few experimental facts known about the

hetarynes is gratifying. However, the above onlering of stabilities is initially

puzzling. An explan.

of this stability sequence must begin with a review of what is known of the electronic structure of the dehydrobenzenes themselves,!° When two hydrogen atoms are removed from the eromatic ring, two orbitals may be Picturedas remaining. These orbitals each formally contain one electron, and they ?are termed the radical lobes mj ond ng. The radical lobes can be combined to form wavefunctions njtng and nj - np, which ore respectively symmetiic (6) ond antisymmetric (A) with respect to the two-fold rotation which interchanges ny and ng « Inthe absence of any interaction, nj + my ond ny = ny are degenerate. Direct overlap between ny ond ny (through-space) ond indirect Interaction with other 7 and 7Srbitals (through-bond) removes the degeneracy of the $ and A molecular orbitals. The mognitude of the energy spitting between $ ond A is a direct meosure of the quantum-mechanical interaction. It is of controlling influence as to whether the ground state of the dehydrobenizene should be a singlet or 6 triplet state.

The magnitude ond direetion of the calculated splittings were suprising

we found S below A by 1,52.and 0.92 eV

Thus for ortho- end meta- benzy

respectively; while for paracbenzyne A wos below § by 1.44 eV. These nsvlt

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together with other unexpected splitting pattems led us to an interpretation of each

splitting os © superposition of o direct through-spoce coupling and an indirect

through-bond coupling, The through-space coupling always puts the positive over=
lop combination at @ lower energy. This maybe $ or Adopending on whether

the radical lobes ore in o cis- or a frans-arrangement. The through-bond coupling

leads to a lower A level when the radical lobes are separated by an odd number of
?7 bonds, and fo lower S level when they are separated by an even number of
T bonds !°

We will construct two models for the analysis of the energy level patterns of

the dehydroazines and dehydrodiazines. In the first model the energy levels of
tially, and the subsequent

ttidehydro~ and tetradehydrobenzenes are considered i
introduction of nitrogen atoms is treated as a small perturbation, ?The second model
tokes the stobility ordering of the monodehydropyridine intermediates, and treats
the subsequent dehydrogenation as o small perturbation,

There are three tridehydrobenzenes, each having three nearly non-bonding
molecular orbitals. The tridehydrobenzenes ean be labelled 123, 124, and 135 in

?on obvious notation, and the non-bonding orbitals designated as X) 1 Xp, and

?Xq in order of increasing energy, os below.

---Page Break---

135

10.59 eV A

-.s9 + 5

112.535 @

The wave functions X con be

classified es $ or A under the two-fold rotation interchanging orbitals 1 ond 3

tn 128 end 135. For 124 thor smo two-fold ans, so thatthe bites are

simply C'-orbitals,

We would anticfpate that the molecular orbitals formed from the radical

lobes mj 4 np 4 nd ng in 123 should fall into a typical ellylic pattem

Xs vom = ene

ng S

% ~ my = ny A

Ho ~ 4 + olny 4 ng s

and this they do. For instance, 1 is cbout 94% localized on atoms 1, 2, ond

3 yore hos the following coefficients (xls normal to the meleculor plon

ahd ?y-axis clong Co Ce) @ to the molecular plane

4 @P,) 0.4205 ?).) 0,000

1 @p,) 0.2000 ep) 0.5499

ej @) 0.1262 en) 0.0474

© al.) ~ 0.4205

?3(@py) 0.2000

2302) 0.1262

The molecular orbitols % , Xp ond Xg of 123 can therefore be sketched

8 follows

---Page Break---

lo

?The splitting pattems found for the benzynes indicated that for an ortho~interaction of two radical lobes the $ combi

was stabilized with respect to the A com=

bination, for @ mats-interuction the S combination wos also favored, wheroos for
© parg ?interaction the A combination was favored. From the above diagram we
see that %X hos two favorable (6) ortho-interactions (ny: ng and ng: ng)
and one favorable (S) mete-interaction (ny :ng)» ??%g has one unfavorable
(A) mete-interoction, while Xg has two unfavorable (A) ortho-interactions, ond
?one favorable (5) meta-intoroction, By Using the symbols (+) ond (-) for
favorable ond unfavoruble interactions, we can summarize the energetics of the

?obove Interactions os

X% - + °
% ° 9° o
% + + °
For the molecule 124 the orbitals %, , Xp ond Xq ore less stoight=

forward fo construct, A logical epproach is to generate the orbitals by ellowing the combinations nj £ ng tointeract with ng. The primary interaction is

---Page Break---

-0-

token ot a though-bond coupling of nj ond ng which places © combination

n= m4 (A) below ny + m4 . Thi corosponds to the stabilization of the A

combination by the poro-interaction in the benzynes, and the fact that the mete

Interection between np ond ng should be much weaker. The uival interaction

tule, derived from perturbation theory, it invoked - namely if two orbitals interact,

the lower mixos in the upper in a booding woy,

but the upper mixes inthe lower tn an entibonding manner. This

1s shown below,

6

O- OF

6

---Page Break---

The actual molecular orbitals have the predi

composition

Xs = © (nyo my) + mg

Xp = (en tmz) #04) + (gre boy ~ mg) = emg + m4

xyz elm tm) = my

The interactions may now be enumerated os wos done above for the 123 system, therefore

athe asia pera

%, ° + °

% + - +

Tho oibitals for 135 follow diwetly from symmetry. Three equivalent

symmetrically disposed exbitals must interact to yield a totally symmetric combina~

tion, ond a degenerate orbital pair? the degenerate orbitals may be chosen

erbitrorily, ond the particular combination illustrated below is picked to reflect

symmetry on rotation eround the Cy = C4 axis,

CF

0

x, degenerate X.

3

?The energetics of the interactions in this cose are

orto e's) pom

---Page Break---

Referting back to the extent of the stabilization produced by the ortho-,

meta, and pora-interactions in the benzynes? In terms of the energy splitting produced, gives E (ortho) = 1.52eV, _E (meta) = 0.92 eV, and E (parc) =

1,44 eV. The use of these values, ond the previous interaction schemes, predicts

the following energy ordering for the nine orbitals of 123, 124, and 135:

23) <% 135) Hj 124 X12) < KH l12B) XL (199) <% 123}< 30124

The actual calculated energy values have been given earlier. They are in exoct

?agreement with the above sequence, supporting the analysis of the interoctions.

In the tridehydrobenzene radicals, the radical lobes are each formally

?occupied by one electron. OF greater significance to the present analysi¢ are the

ftidehydrobenzene cations, with two electrons in the non-bonding levele, and,

more importantly, the anions, with four electrons. The total computed energies

for the tridehydrobenzene cottons are

123 ~462.81 eV

24 461.48 eV

a5 7462.06 eV

The stability onlering of these total energies is clearly in qualitative agreement

with the ordering of the one-electron 24 energies. The total energies of the

tWidehydrobenzene anions can be obtained from the cation energy volues by axing

twice the one-electron energy of the eppropriate Xp orbital. Xp of 124 is of much lower energy thon the other Xp orbitals, so that the finel anion energtes

---Page Break---

ore 05 follows

123 483,99 eV

24 404.50 eV

135 483.26 ev

?The importance of the tridelydrobenzene anions is that we now suppose thot the

stability onder is epproximately preserved ifthe isoelectronic substitution is mode

of aN for a C~, to form the didehychopyridines,

wo &

---Page Break---

One of the radical lobes is now fonmally occupied by @ nitrogen lone pair. the stobility ordering E (124) < E (23) <_E (135) for the tridehydrobenzene

?onions thus implies the following grouping of the didchydropyridines, under the

cbove essumption

ABO < OF) CE

A further ordering in each group con be made by simply essuming that the nitrogen preferentially enters the position of highest electron density in the tridehydrobenzene anion. For 123 and 124 these charge dersities ore

123 124

40 that this would predict the ordering A<CCBCD<FK<E.

quite close to the ectual alphabetical ordering obtained by the direct calculation.

We now fum to the second model for the stability sequence of the dehydro pytidines, Table | below compares the energies of the nj + no(S) and nj ~ng (A) molecular orbitals calculated for the benzynes, monodchydropyridines, ond digzines. In the benzynes the radical lobes are each formally occupied by one ines three electrons are shared between tho rodi=

electron, in the monodehydropyt

es the "radical lobes" are fully occupied with four clec~

cal lobes, and in the

trons. For exemple, the ortho~ series is

---Page Break---

Table I: Energies (in eV) of Non-Bonding Orbitels in

meta, and para~

Benzynes, Monodehydropyti

ines, and Diazines.

Benzyne ?Monodehydropyridine Diozine

ortho- 10.19 A 1,00 "A" 712.40 A

s ase 213.39 _s

Lael 0.99

meto~ A "An ?12.58 A

s "s" 213.39

Fl 0.81

pora= -10.37 $ -l0.83 "s" 712.58

HIL.el_ A 713.24 "A" -13.85_ A

JOEL 14 2.Ai 1.67

It should be noted that whereas symmetry requires the relotion cj = t ¢ inthe

molecular orbital oj nj £ ep ng in the benzynes and diazines, there is no such

restraint for the pyridinyl radicals. If ny ison N ond ng ison C, then invariably

tion on N), and

the lower energy orbital has Hejl > leg! (considerable locali

the higher energy orbital has ley! Z le gl. However, the molecular orbitals ore

such that they can be identified es approximately "S" (e} same sign ese) end

"A" (e1 opposite sign to ?2)-

---Page Break---

th alll cases the ortho~ end pore

interactions. The specific trends are not completely understood by us, though it

interactions are greater than the mot

is clear that the relative efficiency of through-space versus through-bond interaction must be involved. Particularly interesting is the greater mognitude of the

"homonuclear" benzyne and

splitting in the "heteronuclear" pyridinyl case over #
diazine splittings. This can be attributed to the separation of the
and N orbital energies before the interaction is "tumed on". In confirmation

of this, we obtain lage splittings in the following molecules, which ore isoclectronite with the benzynes

cond diazine systems results in the upper molecular orbital (A in this ease) being
destabilized less than the upper molecular orbitals for extho- (A) end paro~ (6)

oriented lobes, The consequence is that when two electrons occupy the non-bonding fiazine dicotion

molecular orbitals, os in benzyne, monodehydropytidinyl cation, and

the ortho-tsomer (benzyne) or the paratisomer (pyridiny!, diazine) is the most stable.

---Page Break---

- 61

However, the mete-isomer becomes progressively stabilized relative to the other

isomers by the addition of one, and two further elections. The actual enemgeties

?are summarized in Table 2.

Table 2: Total Energies (in eV) of Benzynes, Monodehydropyridines, and Diczines

© 6 Function of the Number of Non-Bonding Electrons.

2eelectron cose

benzyne pytidinyl * diazine**

° (492.58) 507.76 520.75

fy ~491..99 -507.68 521.45

P 492.37 508.17]

3relectron case

benzyne? diozine*

° (502. 518,75 533.15

m 502.58 518.84 534,03

P ~502.74 517.00) (300g

Arelectron cose

diozine

benzyne ?~

° 512,96

m (513.17)

P -513.11

---Page Break---

Our primary conclusions are based on the results for the neutral pyridinyl

(B-clectron) and neutral diozine (4-electron) systems. The pyridinyl results imply

orientation,

that a lone pair para to a radical lobe is more stable than the met

which is more stable than the ortho-orientation. The diazine results further sug~

?gest a strong destabilization of two adjacent nitrogens (lone potr repulsion?) and

4a stabilization of a meta~interaction of two lone pair orbitals.

We can now examine the didehydropyridine rosulis in the light of the abeve

considerations on lone pair-radical lobe interactions. The number and type of

N-tadical interactions in the various didehydropyridines are listed below.

N -fiodical Interactions

Structure	ortho	meta	pes,
A	°	1	1
B	I	°	I
c	1	1	°
D	1	I	o
E	°	2	o
C	2	°	°

Taking the obove stabilizing effect Pam > meta > ortho , gives the energy sequence

ACBLE<C,DCF. Only the onler of E and C,

D is inconsistent. This ean

be explained by the presence ofa stabilizing ortho radical ?radieal lobe interaction

OF the benzyne type present in C and D, but absent in E.

---Page Break---

Vee now tum fo the dah

fen possible dehydrodiazines exhibit the following stability sequ

CRE &

- 507.55 oV ? 506,83 - 506,74 - 506.63

G '

508.10 - 507.87 -507.39 - 507.05

K L M N

ND ND N>

~ 507.57 - 506,68 -506.43

° P Q

see 3a, WE

---Page Break---

Once again the analysis is two-fold, We begin by considering the three

a

OBO

1234 1235 1245

The molecular orbitals of 1234 and 1245 are essentially determined by symmetry.

tetradehydrobenzenes

We write them as), Po, Pg and by inanorbitrary onder, since

their final energy ordering is not obvious in every case. For 1234 the symbols $

and A refer to the symmetty operation interchanging nj ond ny, and ng

ond ng . For 245 the symbols SS, AA, AS, and SA refer first to the symmetry

eperation interchanging nj and ng, and ng ond ng , then to the symmetry operation interchanging ny ond ny, ond ng and ng. Note the obvious and

not accidental resemblance of t'vc orbitals of 1234 and 12456 the T-orbitals

of a butadiene.

---Page Break---

$s) $14) bts) ea

Of

CG ¢Y og

6 0 @

$, (ss) $,(As) $,(SA) 4, (AA)

The composition ofthe 1235 molecular itl i ot ely predicid, They emerge

from the cateulation resonbling o sot of eyclobutadi

Le & &

$(s) 41s) #,(a) $s)

---Page Break---

We now estimate the favorable and unfavorable interactions for each of

these molecular orbitals as was done for the tridehydrobenzenes.

eri) mete Pore,

? ooo + +

©) $3 -G-) = -

1234 WW G +444 = +

©) Ae + -

6) too + =

1235 ? gs 9 od 0

) fo 0 0 +

6) + +t -

(AA) boo - -

rus 6A) fe - + +

as) Bo +4 = 3

(5) +4 +4 _

---Page Break---

-B-

Recalling that an ortho= of para-interaction is more stabilizing than @ my

interaction, we would predict for 1234 the energy orderin

ra P roy ordering BL < hy < Gy

<b yr wri Zo P, < Py < Gy, endtorias J, < g,

~ d3 < P4-_ These conclusions are confirmed by the calculated eneray

evel orderings (in eV),

1234 1235 1245

-9.78 (S) 9.58 (5) -9.29 (AA)

10.04 (A) 10.59 (A) -U1.49 65)

11,83 (A) -l.78 (5) -I1.55. (SA)

212.72. () 12.76 (8) ?11.97 (AS)

The calculated total energies for the six electron systems which correspond

to the tetradehydrobenzene dianions are

(1234) dionion ~475.39 eV
(1235) dionion 476,00 eV
(1245) dionion ~476.54 eV

The stabilization of 1245 is essentially due to the relatively low energy of its highest cccupied molecular orbital. tn fact, the total energy order 1245 < 1285 £1234 is paralled by the highest occupied level energies -I1 49 < -I0.59

<-10,04, respectively.

---Page Break---

- th

To obtain the didehydrediazines, we proceed to replace two catbon tom

by nitrogen atoms in the tetradchydrobenzene dianions. For each type of diazing the stability sequence presented earlier is completely predicted by the above considerations, that is

(245) < (2H SB

c < oun < os

kK < UM < N

0 <P < @

Placing oll eleven isomers on a single energy scale is difficult, since relative ?weights would have to be axsigned to the effects of radical lobe interactions and lone pair lobe interactions.

The second enalysis, starting from the stabilities of the

pytidinyl radicals, is quite successful in rationalizing the observed trends for

the dehydropyridazines ond pyrimidines (G to N),ds illustrated below. How= every It fails to distinguish among the dehydropyrazines where each isomer hos

two ortho and two meta interactions.

Nitrogen Radical Interactions

Structure ortho mete ora,

6 ° 2 2

H ' 2 1

1 1 2 1

J 2 2 0

K 2 0 2

L ! 2 0

M 2 2 °

N 3 o '

---Page Break---

-B-

We have gone into great detail

the obove qualitative onalysis to illus

trate how the complex computational trends we have observed are understandable

in terms of quolitative molecular orbital arguments. In a

ion to the molecules

?already mentioned, our actual calculations covered o number of other dchydio=

heterocyclics. The results are summarized in Tables 3-5 below, where the hetarynes

?are grouped os 1-2, 1-3, or I-4 diradicols.

Toble 3: 1,2

lehydroaromatics

Splitting Total Electron Densities

Molecule E_ total V) 2E (eV) fox. Ja.

°,

we 492.58 1.52 4,20 4.20

wee 499.77 0.86 3.77 4.25

KOR ~500.60 1.63 4.35 3.97

@E 505.95 til 3.94 4.10

1 4,29 3.94

7 LOL -506.60 54

OS -506.74 0.89 3.98 3.91

~507.55 1.57 4AM 4M

hE

toe -507.87 1.04 3.55 4M

~505.43 0.04 3.81 3.81

---Page Break---

- 6 -

Teble 4: 1, 3-Dehydroaromatics

Splitting Overlap Population Total Electron Densities

Molecule Tool) eee) Thy fe a

IGF 491.99 0.92 0.041 4.21 4.21

NSP -500.13 1.33, 0.034 3.97 4.07

IGP 498.88 0.04 ~ 0.008 3.85 3.85

?or 499.72 0.69 0.047 418 AAS

SP -505.93 LI 0.047 4.01 3.89

?éP -505.29 0,59 0.00! 3.87 3.87

TeP -505.89 0,94 0.046 4.18 4.18

SGP 7506.83 1.15 0.039 3.90 4.02

S6Pr -507.05 0.70 ~ 0.037 3.96 3.41

WSR -2.10 70 0.037 3.81 3.81

?EP 7506.68 0.28 -0.173 4,06 4.06

---Page Break---

Table 5: 1, 4-Didehydroaromatics

Overlap Population Total Electron Densities

Nolecole Frotal (eV) aé lev) Re 7 te

oe 492.37 1.44 -0.119 4.90 4.99

g 500.05 1.43 ~0.108 3.89 4,39

JD 500.99 1.28 -0.110 3.97 4.24

m 506.63 1.22 0.098 3.87 3.87

iy -507.39 1.37 ~0,0% 3.62 4.26

igy 507.57 1.52 -0.097 3.99 3.99

---Page Break---

of the nitrogen lone pairs hos on effect on the energy

Clearly the pos

splitting AE between $ and A molecular orbitals. Of great interest is the fact that there is @ consistent correlation between stability and the magnitude of this one-electron energy splitting. Compare, for example, the dehydropyridines in Tables 3-5. The largest splittings ore essociated with molecules for which we

predict great relative stability. These are 3, 4-dehydropyridine, 4, 5=

dehydropyrazine, ond 4,6-dehydropytimidine, which probably have singlet ground

states.

INTERPRETATION OF EXPERIMENTAL DATA,

We first tum to the experimental evidence avatlable on the stability of the L,2hetarynes. Treatment of a S-halopytidine with a strong base (usually on clyloted amide ion) leads to the 3+ and 4- amino-substituted pyridines, os

shown in the equation below?

x WR, .

ors A RNT/ RZNH ?> oO + oy?

No 2-ominopyridine is cbserved in these reactions, unless the A-posttion is

blocked by en ally! group? 3,4 -didehydropyridine must be the preferred

intermediate in this reaction, rother than the 2, 3-isomer. Natvely, the 2, 3-isomer

would be expected to be more stable, since two electrons from the radical lobes,

together with the attrogen lone pair can be delocalized over three atoms, This

suggestion hos been forwarded, resting on the basis of a Huckel molecular orbital

---Page Break---

6

calculation.? As pointed out in the the

ical anolysis, our extended Hickel

calculations, which are in ogreement with the experimental data, argue egetnet the utility of simple delocolization over the three odjacent atoms, On the cone trary, whenever the nitrogen lone patr is adjacent to the radical lobes, we have seen that the inenmediate experiences a pronounced destabilization,

IF the accepted mechanism of dehydrohalogenation of S-halopystdines is considered? >, two reasons ?emerge for the formation of 3-and 4-aminopyridines, rather than 2aminopyridine, The mechanism is

wey

oro *

sau? to

-4o er =e = a

° es ? oO

WR

Fint of all, the formation of the I, 2-hetaryne necessitates the removal of a proton by the amide ion to form a carbanion. Two carbonions are possible, the 2-pyridiny! ?onion, and the 4-pyridinyl anion. We have calculated the relative stability of these carbanions in the case where X is hydrogen. The results are shown in Teble 6,

end indicate that the 4-carbanion is 0.08 eV (1.9 keal) more stable than the

2-earbanion, Fortunately, recent experimental data confirms this stability entering,

---Page Break---

= 8 -

Table 6: Heteroaromatic Carbanions

E

Porent total (CV)

x 2 529.75 ?

2

oS 3 530,00 =

4 529.83 -

rn 2 -536.04 =

2

oS b 3 ~536.18 _

A 4 ~535.06 _

x

oy 3 -536.78 8.7

4 ~536.85 8.70

a 2 7597.00 9.01

5,

tor. 4 ~537.67 8.94

5 598,07 8.54

S 2 ~537.45 8.81

since base-catalyzed deuterium exchange studies on pyri

?and 3-chloropyridine

indicate that exchange predominates at the 4-position over the 2-position in both

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?60305-"" The carbonions subsequently el nate halide ion to form the 1, 2-hetaryne.

The combination of the preferred formation of the 4-carbanion, which is the precursor of the 3, 4-didehydropyridine, together with the greater stability (0.83 eV or 19 kcal/mole, Table Sof this hetaryne over the 2, 3-didehydropyridine, accounts for the facts. It is worth reiterating that the predominant factor against the 2, 3= hetaryne is the nitrogen lone pair destabilization of the radical Iebes.

In this context, on removal! of the nitrogen lone pair by protonation!* , elkylation?®, or N-oxide fomation'®? "6, deuterium exchange tokes place preferentially at the 2-position, through the respective 2-pyridinyl earbanions. Again these

experimental results

harmony with EHT calculations, since the results of

Toble 6 ii

cate comparcble stability for the 2- and 4- carbantons once the nftro= ?gon lone pair has been protonated.

?Although little information is avatlable on the 1,2-didchydro intermediates

derived from the diazines, some excellent experimental work has recently been

reported on base-cotalyzed deuterium exchange in these molecules!? the helf=

lives (in minutes) obtained for the exchange, using 0.23M sodium methoxide in

Oxdeuteromethonel ot 165°C ore

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Saad ie ey

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Inspection of Table 6 shows again that wit

in each diazine the relative order of

exchange half-lives Is coretly predicted by the corbanion stabilities. The

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= 82+

Comparison of the total energies of carbunfons from different diazines cannot be made,

since the fotal energies are dominated by the relative disposition of the nitregens.

To obtain @ crude estimate of such a stability sequence the anion energies are sub=

tracted from the parent energies in Table 6. This gives the energy ordering

iL < Gy< Ge < < Joe < oy

Although the general trend is reproduced, our calculations reverse the sequence for the 4-pyridezinyl anion and 5-pyrimidinyt anion(but the experimental valve for the former is only epproximate), and for the 4-pyrimidinyl anton and 2-pyraziny! anton (where the experimental half-lives are very close) . Considering the neglect of sol~

ive exchange mechanisms, @ perfect

vent effects, ond the possibility of competi

ly.

Some experimental data is available on the orientation effects in the addi

cogreement is u

tion of nucleophiles to the I,2-dehydro Intermediates. Whereas only one final

le from I, 2-didehydrobenzene, 3, 4-dide hydropyridine could undergo

product is poss

nucleophilic attack at the 3- or 4-positions to give different product. The addition

of ammonia or piperidine to 3, 4~didehydropyridine indicates o preference for

nucleophilic addition at the 4-position.3-5 Previously we have shown thot EHT

electron densities and total energies of the reaction intermediates suecessfully cor~

relate orientation effects in nucleophilic substitution !® The totol election densities

of Table 3 suggest thot for 3, 4-didehydropyridine preferential nucleophilic attack

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should occur at the 4-position, os © consequence of its lower total elect

tron density

(8.97 against 4.35 electrons). In addition, the total energies of the p

?onions confirm this preference. Localizing a hydride ion, chosen es @ model for the amine nucleophile, at the 3- or 4~ radical lobes of 3, A~didehydlropyridine produces respectively the 4- or 3-pyridinyl anion. Since the 3-pyridinyl anion is 0.17 eV more stable than the 4~isomes (Table 2) nucleophilic attack should be preferred a the 4-position. As we have indicated, when both ertentation exterte lead to the same conclusion, we can be confident that they provide a reosoncble ceccount of the observed effects. In this case, the preferred nuclecphilic attack occur ot the A-position. Although no experimental date hos been published, our calculations indicate thot the 3,4-didehydro intermediate derived from the pyridinium ion should undergo preferential nucleophilic addition at the 4-position also. In 3,4=didehydroquinoline the preferred addition tokes place again at the 4=position, which

»

is also reproduced by our calculations.

OF some interest is the exclusive formation of A-substituted products in

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the reaction of S-bromopyri with piperidine. This suggests that the 4,5 didehydropyrimidine intermediate undergoes preferential nucleophilic attack of the 4x, rather than the 5-position. Again, total electron densities and the total ener=

gies of the pyrimidiny! anions are both in egreement with this orientationel effect.

On the bosis of this experimental result, it can be seriously questioned whether the 2, 3edidehydropytidine is not formed during the dehydrohalegenotion of

a

Dholopyridines. As a result of this reaction, the 2-substituted product is formed

exclusively, and it wos therefore argued that 2,3-didchydropyridine woul! have fed

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to the formation of some S-substituted product. In fact, it was concluded that if the

2, 3-hetaryne intervenes, the 3-isomer should be the predominant product, os @ consequence of the electron withdrawal by nitrogen. Objections have been raised to this interpretation, since a strong orientation effect, similar to that found in 4,5-didehydropyrimidine, may be operative.22 Our colculations provide evidence in favor of this objection. Both total electron densities and total energies of the pyridiny! onions predict preferenticl nucleophilic attack at the 2-position, rather

= On the bosis of our calculations, deprotonation of pyridine ot

than the 3-posi

the 3-position is energetically favored over the 2~ and 4=positions. This renders it

rother likely that the 2, 3-didehydropy

ine may indeed be the intermediate in this

reoction, end @ more detailed experimental study of this point seems advisable.

In the dehydrohalogenotion of 4-halopyridazine, two I, 2-didehydro intermediates could be formed, the 3,4~ and 4,5~ didehydropyridazines. Our cal~ culations indicate that the 4,5-isomer should be more stable, egain due to the dominant effect of the lone pair destobilization. Because of the symmetry of the 4, S-isomer, no orientation effects are possible. In the unsymmetrie 3, 4-isomer, nucleophilic attack could lead to either a 3- or a 4~ substitutes product. However, the differences in the total electron densities and in the anion energies ate exceedingly small, ond predict opposite orientations. This suggests that very litts, if any, orientotion effect ts expected for the intermediates from 4-helopyridazine, Unfor=

rental dota is available.

tunately, no expe

The lock of experimental data on the 1, 3-and 1, A-didehydroaromatics prevent us from confirming some of the interesting conclusions reached in these

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calculations.?9 However, there hos been some speculation on the 2, 6-didehycho=

pyridine as a reaction intermediale. ? Agai

predict this I, 3-dehydro system fo be stabilized by conjugation with the nitrogen one pair. ta eur EHT calculations, and the ottendant theoretical analysis, the 2, b-isomer clearly eimerges as the least stable of the six possible hetorynes formed from pyridine (AF). Once egain, we attribute this finding to destabilization by the nitrogen lone pair, since even the 3,5-isomer (E) in which the lone pair is furthest from the rodical lobes is energetically favored by 0.84 eV over the 2,6-isomer. This provides an explanation of the failure of all reported attempts

to generate this species.2

The effect of the nitrogen lone pair is also revealed in an Interesting way

in the 1, 3-overlap populations. Except in those instances where the lone poi flonked by the radical lobes, the I,3-overlop populations are all small but positive, cond close to that of I,3-benzyne. In 2,6-didehydropyridine, 2, 4-didehydropytt= midine, ond 2,6-didehydropyrazine, where the nitrogen flanks the radical lobes, the overlap populations are stll small, but more significantly of negative sign.

n of the 1, 3-radical

lobes. It is interesting to find that protonation of the nitrogen lone patr in 2,6=didehydropyridine ogain results in a slightly positive |, 3-overlap population, therefore restoring the direct, through-space interaction found in I, 3-didehydrobenzene.

Recently we have noted o preliminary account pf semiempirical SCE calculations on the hetarynes by Yonezowa, Konis! i, and Kato,? which we would like to fo bring to the reader's attention. These calculations ore able to decide if the ground stote of the molecule is in fact o singlet, something which our calculetions aro not able fo do.

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