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A Quantum Theoretical Study of Some N-Heteroaromatic Compounds[1]

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RECEIVED JUNE 7, 1962

A series of N-heteroaromatic compounds including pyrrole, pyridine, pyrimidine and purine are studied within the framework of the ASP-LCAO-MO-SCF procedure and the pi-electron approximation. The further assumption of zero differential overlap is invoked. The semi-empirical parameters are obtained from the most recent values of valence state ionization potentials and electron affinities. Particular attention is focused on reactivity indices; structure is considered to the extent that it influences these values. Two-center repulsion integrals over atomic orbitals are calculated theoretically. Not only has the ground state been considered, but also the lowest triplet ($\pi \rightarrow \pi^*$) and the doublet anion have been treated as well. These latter states are calculated directly using the Adams and Lykos implementation of the Roothaan open-shell theory. Ground state virtual orbital densities are compared with those resulting from the open shell calculation. Electron densities, spin densities and frontier electron densities are all reported, and these are compared with observed reactivities where experimental data permit.

Introduction

The general method adopted in this work has been to consider a series of compounds, each presenting certain selected new features such that when viewed collectively these would constitute a basis for discussing the purine molecule. The calculations were all carried out within the theoretical framework set forth in the Adams and Lykos[4] implementation of the Roothaan open-shell treatment.[5] Involved is the use of single determinantal wave functions for both the ground and the excited states considered, the pi-electron approximation[6], the Goeppert-Mayer and Sklar expansion of the core potential, and their evaluation of one-center core integrals using the valence state ionization potential, W_{2p}.[7] We also use the Pariser and Parr assumption of zero differential overlap (ZDO), and adopt the method they suggest for the calibration of one center coulomb integrals.[8,9] Appropriately scaled Slater-type $2p\pi$ atomic orbitals (STO's) have been used and the two center repulsion integrals that arise are evaluated theoretically.[10] In obtaining the semi-empirical parameters, the most recent values of Pritchard and Skinner[11] have been used. Thus the two-electron, one-center repulsions have been recalculated and the orbital scale factor adjusted consistent with these new values.

In the calculation done on the open-shell systems, the problems were respecified and results obtained without reference to the ground state solutions. For the purpose of comparison, we have reported electron densities and spin densities obtained from both the open shell method and those that result from using the orbitals generated in the ground state solution. In all cases we have taken the molecules to be planar, and in the case of the excited states we have used the same geometry as the ground state. A calculation on naphthalene has indicated,[12] that this may not be entirely justified.

The series of molecules to be discussed includes pyridine, pyrimidine, pyrrole and purine. The details with respect to the selection of geometry and the evaluation of the integrals are discussed in the next sections.

Molecular Geometries

The initial attempt to specify geometry was based on the *a priori* idea that bond orders could be correctly translated into bond lengths and yield an energy minimum. A calibration was carried out (neglecting overlap) based on the 1.27 Å. length of the pure, (*i.e.*, pi bond order equal to one), carbon–nitrogen double bond in dimethylglyoxime,[13] and the benzene-like, (*i.e.*, bond order of two thirds), carbon–nitrogen bond in pyridine. The pyridine carbon–nitrogen bond recently has been determined accurately.[14] The resulting linear form is

$$r = 1.478 - 0.208\,p$$

in which r is the internuclear separation in Å., and p is the pi bond order to be discussed in the next section. A similar expression was obtainable readily for carbon–carbon bonds,[15] and is given by

$$r = 1.511 - 0.173\,p$$

In principle one could assume some initial geometry, compute bond orders, infer a new geometry and iterate to self consistency in bond lengths. Hopefully the geometry corresponding to the energy minimum might be obtained in this manner. Table I indicates that so long as one deals with molecules where all the atoms are in the same valence state, good results are obtained. In this tabulation we have compared those bond lengths calculated from the bond order expressions given above with observed bond lengths. For the case of pyrimidine, the geometry was synthesized from the carbon–carbon length in benzene and the carbon–nitrogen length in pyridine. This model is in reasonable agreement with lengths suggested by Spencer using an extrapolation technique.[16]

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(1) Presented at the 141st National Meeting of the ACS, March, 1962, and based on part of the research work undertaken by R. L. Miller in partial fulfillment of the requirements for the Ph.D. degree at Illinois Institute of Technology.

(2) University of Illinois, Navy Pier, Chicago.

(3) Supported in part by a grant from the National Institutes of Health.

(4) O. W. Adams and P. G. Lykos, *J. Chem. Phys.*, **34**, 1444 (1961)

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(6) P. G. Lykos and R. G. Parr, *J. Chem. Phys.*, **24**, 1166 (1956).

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(8) R. Pariser and R. G. Parr, *ibid.*, **21**, 466 (1953).

(9) R. Pariser and R. G. Parr, *ibid.*, **21**, 767 (1953).

(10) C. C. J. Roothaan, *ibid.*, **19**, 1445 (1951).

(11) H. O. Pritchard and H. A. Skinner, *Chem. Revs.*, **55**, 745 (1955).

(12) H. N. Schmeising, presented at the 141st ACS Meeting, March, 1962.

(13) L. Merritt and E. Lanterman, *Acta Cryst.*, **5**, 811 (1952).

(14) B. Bak, K. Hansen-Nygaard and J. Rastrup-Andersen, *J. Mol. Spect.*, **2**, 361 (1958).

(15) M. J. S. Dewar and H. N. Schmeising, *Tetrahedron*, **5**, 166 (1959).

(16) M. Spencer, *Acta. Cryst.*, **12**, 59 (1959).

TABLE I

Bond lengths as obtained from bond orders for pyrrole, pyridine, and pyrimidine and compared with observed bond lengths (all expressed in angstrom units). See figure one for the numbering system used.

	Pyridine		Pyrimidine		Pyrrole	
Bond	Calcd.	Obsd.	Calcd.	Obsd.[a]	Calcd.	Obsd.
1–2	1.340	1.340	1.344	1.340	1.406	1.383
2–3	1.398	1.395	...	....	1.359	1.371
3–4	1.395	1.394	1.341	1.340	1.439	1.429
4–5			1.397	1.397		

[a] This model was synthesized as described in the text.

Since bond orders are not a valid index of geometry for cases in which pyrrole-nitrogens occur in the molecule, some other criterion is required for systems containing this atom type. Two sets of geometries for pyrrole have been reported,[17,18] one much more recent than the other. We used these to test whether a pi-electron calculation and a sigma compression energy calculation[19] might be used to select geometry. Table II displays the results of these determinations, and indicates that the model proposed by Bak, *et al.*,[18] is energetically the most favorable, thus tending to validate the method. All subsequent calculations on pyrrole correspond to Model B of Table II.

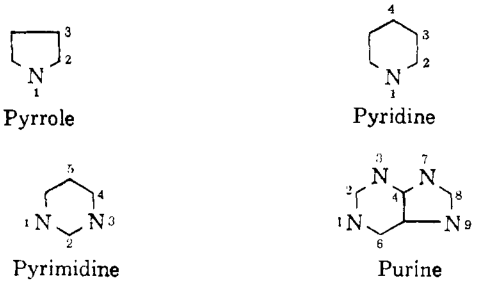

Fig. 1.—The numbering system adopted in the present calculation.

TABLE II

The determination of the "best" molecular geometry for the pyrrole molecule. Model A is due to Schomaker and Pauling (1939), and model B is due to Bak, *et al.*[18] All bond lengths are in Å. Refer to figure one for the numbering system used.

	Model A	Model B
N1–C2	1.42	1.383
C2–C3	1.35	1.371
C3–C4	1.44	1.429
Pi-energy, a.u.	−7.0899	−7.0932
Compression energy, a.u.	0.0572	0.0453
Net (a.u.)	−7.0327	−7.0479
Difference (kcal. mole^{-1})		−9.5

Essentially the same procedure as described above for the case of pyrrole may be used to make a choice between the two possible tautomeric structures for purine. The results listed in Table III indicate that the hydrogen should be properly placed at N7 with respect to the numbering system of Fig. 1. Further, the difference in energy between these systems seems reasonable in terms of probable experimental differences of energy between tautomeric forms. Finally, such a placement corresponds to the form found on the basis of experiment.[20] The geometry used in the present calculation of the purine molecule is given in Table III and is compared with the values obtained by Cochran,[20] in his X-ray determination of the structure of the related compound adenine. The results of calculations on the imidazole system were inconclusive; thus an averaged set of bond lengths was adopted for this portion of the molecule.

TABLE III

Bond lengths adopted for the purine molecule compared to those obtained by Cochran for adenine.[20] The pi-energies are for the two possible tautomers of the molecule. All lengths are expressed in angstrom units. Refer to figure one for the numbering system.

Bond	Present work	Adenine values
N1–C2	1.37	1.37
C2–N3	1.30	1.30
N3–C4	1.36	1.36
C4–C5	1.37	1.37
C5–C6	1.40	1.40
C6–N1	1.38	1.38
C5–N9	1.37	1.37
N9–C8	1.34	1.35
C8–N7	1.34	1.33
N7–C4	1.37	1.36
Pi-energy (a.u.) with pyrrole nitrogen at N9		−15.145
Pi-energy (a.u.) with pyrrole nitrogen at N7		−15.220

Method of Calculation

The wave function for the pi-electronic system is represented as a single determinant; thus the Pauli principle is satisfied, and no configuration interaction is included. Rather than use Hückel orbitals which are non-optimal for the single determinant and to correct for this error in part by invoking configuration interaction, we have elected to find optimal orbitals for the single determinant (SCMO) and to defer the question of seeking optimal orbitals within an extended Hartree–Fock method. The relative validity of the present approach with respect to ground state calculations as compared to other possibilities has been discussed by McWeeny.[21]

Each member of this anti-symmetrized product (ASP) is a spin factored molecular orbital (MO)ψ_i, which is constructed as a linear combination (LCAO) of STO's, χ_r. Thus

$$\psi_i = \sum_r \chi_r c_{ir} \tag{1}$$

The total spin free Hamiltonian operator H, for the system expressed in atomic units is given by

$$\mathrm{H} = \sum_i H_{\mathrm{core}}(\mathrm{i}) + \frac{1}{2}\sum_{\mathrm{ij}} 1/r_{\mathrm{ij}} \tag{2}$$

where r_{ij} is the distance between the electrons i and j, and H_{core} (i) may be written as

$$H_{\mathrm{core}}(\mathrm{i}) = T(\mathrm{i}) + \sum_r U_r(\mathrm{i}) \tag{3}$$

Here, T(i) is the kinetic energy of the ith electron and U_r(i) is the potential that this electron ex-

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[17] V. Schomaker and L. Pauling, *J. Am. Chem. Soc.*, **61**, 1769 (1939).

[18] B. Bak, D. Christensen, L. Hansen and J. Rastrup-Andersen, *J. Chem. Phys.*, **24**, 720 (1956).

[19] M. J. S. Dewar and H. N. Schmeising, *Tetrahedron*, **11**, 96 (1960).

[20] W. Cochran, *Acta Cryst.*, **4**, 81 (1951).

[21] R. McWeeny, *Proc. Phys. Soc.*, **A70**, 593 (1957).

periences due to the *r charged* atoms of the molecular core. In equation 3 we have neglected the effects of the uncharged hydrogen atoms of the sigma structure.[22]

The quantities of principal interest in the present work are the pi-electronic densities, q_r, and the bond orders p_{rs}, defined,[23] respectively, by

$$q_r = \sum_i n_i (c_{ir})^2$$

$$p_{rs} = \sum_i n_i c_{ir} c_{is}$$

The sums are to be taken over the i occupied molecular orbitals, n_i is the electron occupancy of the particular MO, and p_{rs} is defined for r and s neighbors only.

Specifically we require the c_{ir} in the above expressions. These result from the solution of the Roothaan equations having the *form* (for either open or closed shells),

$$Fc_i = \epsilon_i c_i$$

F is the Hartree–Fock Hamiltonian and its explicit form has been elaborated within Z.D.O. by Adams and Lykos.[4] In the construction of this operator, and using equations 1 and 2, the following integrals over STO's arise

$$\alpha_r = \langle \chi_r(i) | H_{core}(i) | \chi_r(i) \rangle$$
$$\beta_{rs} = \langle \chi_r(i) | H_{core}(i) | \chi_s(i) \rangle$$

and

$$(pq/rs) = \langle \chi_p(i)\chi_r(j) | 1/r_{ij} | \chi_q(i)\chi_s(j) \rangle$$

In accordance with equation 3, we may expand α_r as

$$\alpha_r = \langle \chi_r(i) | T(i) + \sum_s U_s(i) | \chi_r(i) \rangle \quad (4)$$

The sum in equation 4 may be rewritten as

$$\sum_s U_s(i) = U_r(i) + \sum_{s \neq r} \left[U_s^*(i) - N_s \int |\chi_s(j)|^2 \frac{d\tau_{ij}}{r_{ij}} \right] \quad (5)$$

Here $U_s^*(i)$ is the potential due to the *uncharged* atom s of the core and the integral represents the charge distribution of the N_s electrons associated with this center in going from the charged to the uncharged form. This last factor, introduced into the theory by Pople,[24] we find of considerable importance. It has been treated as an optional parameter by Brown and Heffernan[25] in their work on pyrrole (this by recalibration of β), not mentioned in the recent calculation of Pullman,[26] and included in the paper by Grabe.[27] If one uses the "standard" β values as defined below, inverted reactivity orders are obtained when N_s is ignored in the cases of pyrrole and purine, as is shown in Table IV.

If one now invokes the W_{2p} approximation, consistent with the Goeppert–Mayer and Sklar method[7] and uses the expansion of equation 5 in the evaluation of alpha, one obtains

$$\alpha_r = W_{2p} - \sum_{r \neq s} [N_s(ss/rr) - (s/rr)]$$

TABLE IV

A comparison of self consistent electron densities for the ground states of the pyrrole and purine molecules. Method I ignores the core effect of the two pi-electrons on the pyrrole-nitrogen, Method II takes this into account as indicated in equation 5.

	Pyrrole		Purine	
Position	Method I	Method II	Method I	Method II
1	1.949	1.811	1.357	1.270
2	0.807	1.055	0.862	0.794
3	1.218	1.040	1.254	1.240
4	...	...	0.646	0.943
5			1.043	1.051
6			0.895	0.781
7			1.935	1.780
8			0.620	0.910
9			1.388	1.231

The first of the two kinds of integrals entering in the summation is a two-center repulsion type and the second, a penetration type. Table V summarizes the valence state ionization potentials W_{2p} used in the present calculation for the three kinds of atoms present. The penetration integrals have been evaluated with an exponential fit in which we assign the value 0.8 ev. for nearest neighbor distances (1.40 Å.) and 0.1 ev. for second neighbors. As indicated above, the effect of the neutral hydrogen atoms was not included. This corresponds roughly to the values chosen by Moser,[28] in a calculation done on the ground state of naphthalene.

The integrals, β have been calibrated after the fashion of Pariser and Parr[8,9] using the form

$$\beta_{rs} = A \exp(-bR_{rs})$$

where R_{rs} is the internuclear separation between atoms r and s. If r and s are not nearest neighbors then β has been set equal to zero. For carbon:carbon and carbon:pyridine–nitrogen interactions, we have used values of A and b so that the Pariser and Parr β values might be obtained. For the carbon:pyrrole–nitrogen system, A and b have been selected so as to reproduce the β value reported by Dewar and Paoloni in their study of melamine.[29] Table V lists the particular A's and b's used in this work.

As a consequence of ZDO all integrals of the form (pq/rs) vanish except those for which $p = q$ and $r = s$. The one-center integrals of this type (pp/pp) were obtained from the appropriate valence state ionization potentials and electron affinities. Once these one-center, two-electron integrals were available, using an expression suggested by Paoloni,[30] the orbital exponent Z was obtained easily from

$$(pp/pp) = 5.324Z$$

As already has been indicated, the remaining two electron integrals were all calculated theoretically.

The calculations were carried out using a general program written mainly by H. N. S. Convergence to self consistency was assumed to obtain when the largest change in a linear coefficient was 10^{-4} for one iteration. The input data consisted of

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(22) I. Fischer, *Arkiv Fysik*, **5**, 377 (1952).

(23) C. A. Coulson, *Proc. Roy. Soc.* (*London*), **A169**, 413 (1939).

(24) J. A. Pople, *Trans. Faraday Soc.*, **49**, 1375 (1953).

(25) R. D. Brown and M. L. Heffernan, *Aust. J. Chem.*, **12**, 319 (1959).

(26) B. Pullman and A. Pullman, *Compt. rend.*, **253**, 2277 (1961).

(27) B. Grabe, *Arkiv Fysik*, **17**, 97 (1960).

(28) C. M. Moser, *J. chim. phys.*, **52**, 24 (1955).

(29) M. J. S. Dewar and L. Paoloni, *Trans. Faraday Soc.*, **411**, 261 (1957).

(30) L. Paoloni, *Nuovo Cimento*, **4**, 410 (1956).

specifying the appropriate bond lengths, bond angles and designating the atoms of the core as carbon, pyridine-nitrogen or pyrrole-nitrogen. In the ground state determinations, usually six or seven iterations were sufficient; for the excited states in some cases as many as twenty were required.

Reactivity Indices

In Table VI we report the values obtained for the electron densities for the ground states of the various molecules studied. For the sake of comparison, Table VII lists the frontier electron densities[31] obtained as well. For the cases of pyridine and pyrimidine the results here are in qualitative agreement with experimental findings,[32-34] and those reported previously by Peacock[35]; in contrast to these latter, the electron densities arising from the present calculation give a somewhat larger spread. The results reported for pyrrole are in qualitative agreement with those of Brown and Heffernan,[25] who used their variable electronegativity method. As has been reported previously,[36] the results for purine agree very well with experimental data, and predict correctly the order of nucleophilic attack on carbons two, six and eight as well as the relative basicity of nitrogens one and three. From these tables, it is clear also that the self-consistent electron densities and the frontier electron densities predict the same qualitative order of substitution.

TABLE V

Values of the parameters used in the present calculation. W_{2p} is the valence state ionization potential. The one-center, two-election integral is designated (pp/pp). Z is the effective nuclear charge. In the β fit, A is the linear parameter and the exponential has been chosen as 2.6497 for all cases. The units are as indicated.

Atom	W_{2p}, ev.	(pp/pp), ev.	$Z/2$	A, au.
C^+	11.42	10.84	1.018	−92.521
N (pyridine)$^+$	14.23	12.93	1.214	−86.818
N (pyrrole)$^{++}$	27.73	14.24	1.337	−70.678

TABLE VI

Self-consistent electron densities for the ground states of pyrrole, pyridine, pyrimidine and purine. See figure one for the numbering system adopted.

Position	Pyrrole	Pyridine	Pyrimidine	Purine
1	1.811	1.194	1.235	1.270
2	1.055	0.881	0.776	0.794
3	1.040	1.052	...	1.240
4	...	0.941	0.825	0.943
5	...	...	1.103	1.051
6			...	0.781
7				1.780
8				0.910
9				1.231

TABLE VII

Frontier electron densities for the ground states of pyrrole pyridine, pyrimidine and purine; HOMO refers to the highest occupied molecular orbital and LEMO to the lowest empty molecular orbital. See Figure 1 for the numbering system.

Position	Pyrrole		Pyridine		Pyrimidine		Purine	
	HOMO	LEMO	HOMO	LEMO	HOMO	LEMO	HOMO	LOMO
1	0.0	0.094	0.0	0.228	0.054	0.181	0.008	0.167
2	.344	.317	.235	.120	.190	0.0	.129	.019
3	.156	.136	.268	.071	...	...	.059	.118
4	...	...	.0	.390	.114	.318	.177	.067
5			...	...	.473	.0	.221	.003
6					...	...	.092	.444
7							.007	.0
8							.200	.102
9							.108	.067

Reactivity Indices for the Triplet States and Doublet Anions.—Spin densities as reported here are defined as

$$\rho_r = \sum_i (c_{ir})^2 \tag{6}$$

where ρ_r is the spin density associated with the rth atom and the sum is taken over singly occupied molecular orbitals. In some cases the ρ_r are scaled by a factor of one-half. This scaling procedure has not been adopted in the present calculation.

The c_{ir} of equation 6 are obtained in two different ways. As is well known, when an LCAO-MO treatment is carried out, as many MO's are generated as there are centers in the core. In particular, when a ground state calculation is performed, one obtains an optimal set of lowest filled molecular orbitals, and as a by-product, an unfilled set, called virtual orbitals (VO). One may then treat the excited triplet state, for example, by promoting an electron from the highest filled orbital to the lowest virtual orbital. A similar procedure may be used in the description of the doublet anion. Applying equation 6, a set of spin

TABLE VIII

A comparison of electron densities for the lowest triplet states of pyrrole, pyridine, pyrimidine and purine; OS refers to values obtained using the open shell method and VO to values obtained from the virtual orbitals generated in the ground state calculation.

Position	Pyrrole		Pyridine		Pyrimidine		Purine	
	OS	VO	OS	VO	OS	VO	OS	VO
1	1.895	1.905	1.205	1.422	1.368	1.363	1.032	1.429
2	1.028	1.027	0.896	0.769	0.551	0.586	0.867	0.684
3	1.021	1.019	0.975	0.855	...	...	1.131	1.299
4	...	...	1.052	1.331	1.043	1.028	1.101	0.846
5			...	...	0.622	0.632	0.972	0.833
6					...	...	0.998	1.133
7							1.747	1.773
8							0.923	0.812
9							1.230	1.190

TABLE IX

A comparison of electron densities for the doublet anions of pyrrole, pyridine, pyrimidine and purine; OS refers to values obtained using the open shell method and VO to values obtained from the virtual orbitals generated in the ground state calculation.

Position	Pyrrole		Pyridine		Pyrimidine		Purine	
	OS	VO	OS	VO	OS	VO	OS	VO
1	1.887	1.906	1.430	1.422	1.394	1.417	1.430	1.437
2	1.382	1.371	0.982	1.001	0.823	0.777	0.816	0.813
3	1.171	1.176	1.113	1.123	...	...	1.396	1.358
4	...	...	1.317	1.333	1.165	1.113	1.033	1.022
5			...	...	1.058	1.103	0.984	1.054
6					...	...	1.214	1.226
7							1.786	1.780
8							1.095	1.012
9							1.217	1.298

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[31] K. Fukui, T. Yonezawa and H. Shingu, *J. Chem. Phys.*, **20**, 722 (1952).

[32] W. G. Schneider, H. J. Bernstein and J. A. Pople, *Can. J. Chem.*, **35**, 1487 (1957).

[33] S. Gronowitz and R. A. Hoffman, *Arkiv. Kemi*, **16**, 459 (1961).

[34] G. S. Reddy, R. T. Hobgood, Jr., and J. H. Goldstein, *J. Am. Chem. Soc.*, **84**, 336 (1962).

[35] T. K. Peacock, *J. Chem. Soc.*, 1946 (1960).

[36] R. L. Miller and P. G. Lykos, *Tetrahedron Letters*, **11**, 493 (1962).

TABLE X

A comparison of spin densities for the lowest triplet state of pyrrole, pyridine, pyrimidine and purine; OS refers to values obtained using the open shell method and VO to value obtained from the virtual orbitals generated in the ground state calculation.

Posi-	Pyrrole		Pyridine		Pyrimidine		Purine	
tion	OS	VO	OS	VO	OS	VO	CS	VO
1	0.105	0.094	0.212	0.228	0.255	0.235	0.846	0.416
2	.773	.661	.366	.353	.137	.190	.002	.132
3	.174	.292	.339	.339	...	...	.139	.210
4	...	...	.369	.390	.428	.432	.106	.277
5			...	...	.496	.472	.003	.261
6					...	...	.856	.228
7							.016	.116
8							.007	.200
9							.027	.161

TABLE XI

A comparison of spin densities for the doublet anions of pyrrole, pyridine, pyrimidine and purine; OS refers to values obtained using the open shell method and VO to values obtained from the virtual orbitals generated in the ground state calculation.

Posi-	Pyrrole		Pyridine		Pyrimidine		Purine	
tion	OS	VO	OS	VO	OS	VO	OS	VO
1	0.113	0.094	0.200	0.228	0.187	0.181	0.178	0.167
2	.328	.317	.079	.120	.0	.0	.017	.019
3	.116	.136	.082	.071	...	...	.088	.118
4	...	...	.476	.390	.313	.318	.061	.067
5			...	...	.0	.0	.0	.003
6					...	...	.561	.444
7							.0	.0
8							.048	.102
9							.045	.067

densities may be obtained from the ground state determination. This has been done and the results are compared with those spin densities calculated when the open-shell procedure is used. In the latter case no explicit reference (except for geometry, as indicated above) is made to the ground state of the system of interest. Tables X and XI list these values.

Only scant experimental evidence is available so that it is not possible to make a judgment as to which method is to be preferred. Carrington and dos Santos-Veiga, in a recent electron spin resonance study of the anions of N-heteroaromatics,[37] point out that both pyridine and pyrimidine anions appear to dimerize. They state that for the case of the pyridine system, reaction occurs at the four position, which is the result that would be predicted on the basis of the present calculation.

Using the definition of electron density set down in the last section, and using the two methods outlined above, we have also calculated the electron densities of the lowest triplet and doublet anions of these molecules. These results are found in VIII and IX.

For the case of the electron density, it is seen that both methods predict the same relative reactivity. In the case of the spin densities, reasonable agreement between the two methods is evident except for the purine triplet where rather large differences appear.

Acknowledgment.—We wish to acknowledge a generous grant of Univac 1105 time made available by the Illinois Institute of Technology, and several useful discussions with Dr. R. L. Flurry and Mr. D. James of this department.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WISCONSIN, MADISON, WISCONSIN]

Solute–Solvent Interactions in the Radiolysis of Alkyl Halide–Pentane Solutions[1]

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RECEIVED JUNE 25, 1962

The G values for production of methyl, ethyl, propyl and pentyl radicals by the radiolysis of 0.25 mole % solutions of iodine in pentane are reduced by the presence of methyl iodide, ethyl iodide or normal propyl bromide at concentrations in the range of 1%, except for the radical representing the hydrocarbon fragment of the alkyl halide. The latter is produced with high yield. The total G (radicals) is increased from 8.2 to about 11.6 by the halide additives. The presence of normal propyl chloride does not produce these effects. Studies of the fate of $C^{14}H_3$ radicals produced in the radiolysis of $C^{14}H_3I$ solutions in pentane and of the fate of I^{131} from similar $C_2H_5I^{131}$ solutions have been used to examine further the solute–solvent interactions during radiolysis. The evidence indicates that the reaction $RI + e^- \rightarrow R + I^-$ must play a significant role in such systems and supports the conclusion that neutralization of RH^+ ions by negative ions is less apt to lead to radical production than neutralization by electrons. Electron capture and any other indirect processes which may lead to $C^{14}H_3$ production during radiolysis of solution of $C^{14}H_3I$ in pentane increase in yield with increasing concentration below about 0.8 mole % and remain constant at higher concentrations, indicating that all available electrons and other radical producing species react with the halide at this concentration. Iodine production occurs during the radiolysis of ethyl iodide pentane solutions in which only 10% of the energy is absorbed by the ethyl iodide. This reflects solute–solvent interactions since G (radicals) in the radiolysis of pentane is 8.2 while $G(^1/_2I_2)$ in the radiolysis of C_2H_5I is 4.2.

Introduction

There are two significant reasons for studying the radiolysis of dilute solutions of alkyl halides in hydrocarbons. One is the possibility that such studies may yield evidence for the reaction

$$RI + e^- \longrightarrow R + I^- \qquad (1)$$

thus supporting the concept that electrons ejected from solute molecules escape from the parent positive ion rather than returning immediately to it under the influence of the coulombic field. The second reason is to explore reactions other than (1) which may result from solvent–solute interactions, for the purpose of gaining improved understanding of the mechanism of hydrocarbon radiolyses. The first goal was initially suggested and attempted by Williams and Hamill[2] using several solutes with

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[1] (a) Presented before the Division of Physical Chemistry at the September 1961 meeting of the American Chemical Society at Chicago, Illinois; (b) Additional details of this work are given in the Ph.D. thesis of Paul R. Geissler, University of Wisconsin, 1962, available from University Microfilms Ann Arbor, Michigan.

[2] R. R. Williams and W. H. Hamill, *Radiation Research*, **1**, 158 (1954).