Landau, *Phys. Z. Sowjetunion*, **2**, 46 (1932); (c) G. W. Robinson and R. P. Frosch, *J. Chem. Phys.*, **37**, 1962 (1962); (d) *ibid.*, **38**, 1187 (1963); (e) J. Jortner, S. A. Rice, and R. M. Hochstrasser, *Adv. Photochem.*, **7**, 149 (1969); (f) J. Jortner, *Pure Appl. Chem.*, **27**, 329 (1971).

(12) An ^3O intermediate is described by a wave function having major charge transfer ($^3D^+A^-$) and diexcitation ($^3D^*A^*$) contributions.

(13) D. Grimbert, G. Segal, and A. Devaquet, *J. Am. Chem. Soc.*, **97**, 6629 (1975).

(14) The reaction polarity is defined as $(I_D - A_A)^{-1}$, where I_D is the ionization potential of the donor reactant and A_A is the electron affinity of the acceptor reactant.

(15) (a) N. J. Turro and P. Lechtken, *J. Am. Chem. Soc.*, **94**, 2886 (1972); (b) H. C. Steinmetzer, A. Yekta, and N. J. Turro, *ibid.*, **96**, 282 (1974); (c) N. J. Turro, P. Lechtken, G. Schuster, J. Orell, H. C. Steinmetzer, and W. Adam, **97**, 1627 (1975); (d) N. J. Turro and A. Devaquet, *ibid.*, **97**, 3859 (1975); (e) N. J. Turro, V. Ramamurthy, K. C. Liu, A. Krebs, and R. Kemper, *ibid.*, **98**, 6758 (1976); (f) T. R. Darling and C. S. Foote, *ibid.*, **96**, 1625 (1974).

(16) (a) L. Salem and C. Rowland, *Angew. Chem., Int. Ed. Engl.*, **11**, 92 (1972); (b) L. Salem, *Pure Appl. Chem.*, **33**, 317 (1973).

Qualitative Potential Energy Surfaces. 4. Aromatic Substitution

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Abstract: Qualitative potential energy surfaces for electrophilic, photoelectrophilic, nucleophilic, and photonucleophilic aromatic substitutions are constructed and selection rules are derived. It is predicted that the regiochemistry of electrophilic and photonucleophilic aromatic substitutions is controlled by the electron density of the highest occupied MO of the aromatic substrate. On the other hand, the regiochemistry of nucleophilic and photoelectrophilic aromatic substitutions is controlled by the electron density of the lowest unoccupied MO of the aromatic substrate. The dependence of reaction rate and selectivity on polarity is discussed.

In a previous paper,[1] we outlined a qualitative theoretical method for constructing one-dimensional potential energy (PE) surfaces. We now use this approach in order to derive selection rules for the regiochemistry of thermal and photochemical nucleophilic and electrophilic aromatic substitutions.

I. Theory

A. Singlet Electrophilic Aromatic Substitutions. Consider the reaction shown below, where AY is an aromatic substrate, EX is an electrophile, and (AY-E)$^+$ is the Wheland intermediate.[2]

$$AY + E^+X^- \rightarrow [AY-E]^+X^- \rightarrow products$$

The zero-order basis set configurations which are necessary for describing the addition step of the reaction sequence shown above along with the associated interaction matrix are shown in Scheme I, where AY is assumed to be the donor D and the

Scheme I. Zero-Order Basis Set Configurations and Interaction Matrix for Electrophilic Aromatic Substitutions

electrophile E$^+$X$^-$ the acceptor A. The equations of the corresponding diabatic surfaces are given below and the diabatic as well as adiabatic surfaces are sketched in Figure 1. The meanings of the various symbols of eq 1–3 have been discussed in previous papers.[1]
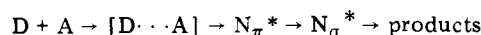
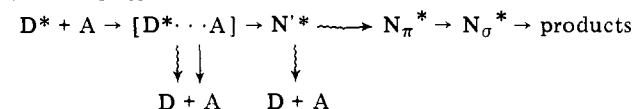$$E(DA) = S(r) \tag{1}$$

$$E(D^+A^-) = I_D - A_A + S'(r) - C(r) \tag{2}$$

$$E(D^*A) = G(\pi\pi^*) + S'(r) \tag{3}$$

The information contained in the adiabatic potential surfaces can be conveyed by means of the chemical equations given below:

Thermal:

$$D + A \rightarrow [D\cdots A] \rightarrow N_\pi^* \rightarrow N_\sigma^* \rightarrow products$$

Photochemical:

$$D^* + A \rightarrow [D^*\cdots A] \rightarrow N'^* \rightsquigarrow N_\pi^* \rightarrow N_\sigma^* \rightarrow products$$

$$\downarrow\downarrow \qquad\qquad \downarrow$$

$$D + A \qquad D + A$$

The ground PE surface exhibits two barriers, E_A and E_B, and two intermediates, N_π^* and N_σ^*, both of which are described by a wave function with major charge transfer contribution. On the other hand, the first excited surface exhibits a barrier E^* followed by an excited intermediate N'* arising from the avoided crossing of the D$^+$A$^-$ and DA diabatic surfaces. This intermediate can decay across the energy gap, ΔQ, and find its way to the ground-state surface. Hereafter, the reaction will take place on the ground surface, and hence its outcome will be determined partly by the properties of this surface.

In the case of the thermal reaction, it is clear that two different situations obtain depending on the relative sizes of the E_A and E_B barriers:

(a) Situations where $E_A > E_B$, i.e., reactions in which formation of N_π^* is rate controlling. These will be referred to as type A reactions.

(b) Situations where $E_A < E_B$, i.e., reactions in which formation of N_σ^* is rate controlling. These will be referred to as type B reactions.

On the other hand, the photochemical reaction is initiated on the lowest adiabatic excited surface, but it is completed on the ground surface. Accordingly, it is impossible to decide in
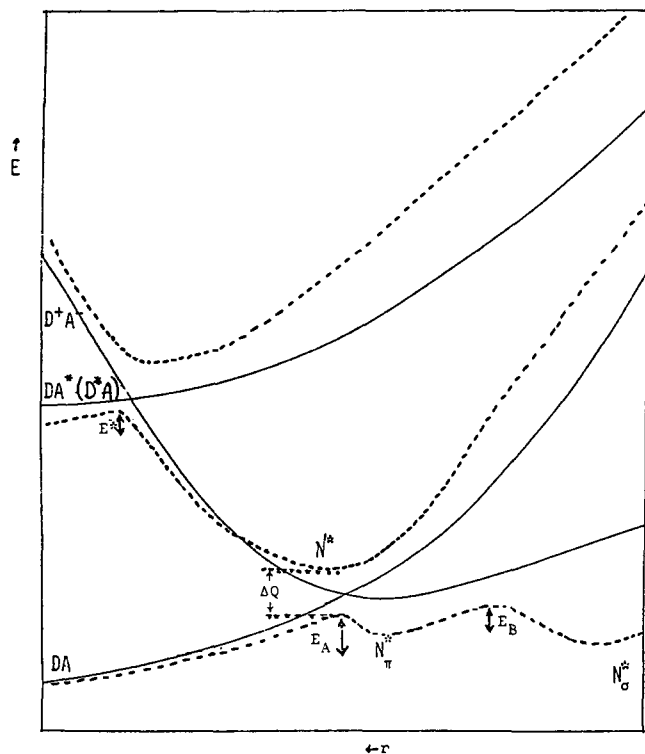
Figure 1. Diabatic (solid lines) and adiabatic (dotted lines) potential energy surfaces for electrophilic aromatic substitutions (D ≡ aromatic substrate, A ≡ electrophile), and for nucleophilic aromatic substitutions (D ≡ nucleophile, A ≡ aromatic substrate). Diagram is schematic.

any simple manner and an a priori sense whether the rate of the photochemical reaction is primarily determined by the features of the lowest excited or the ground surface. Therefore, we shall assume that the rate of the photochemical reaction is controlled by the features of the excited surface as well as the efficiency of the decay from the upper to the lower surface.[3] This assumption is justified since decay may well lead to a vibrationally excited N_π^* intermediate which can readily traverse the E_B barrier.[4] Note that the photochemical reaction will resemble the thermal reaction if decay leads to an N_π^* intermediate which can only collapse to an N_σ^* intermediate in a rate-controlling step.

We are now prepared to utilize the general ideas outlined in a previous paper[1] in order to develop regiochemical selection rules as well as predict the effect of polarity, P, defined by eq 4, on reaction rate and selectivity. The various rules and predictions are stated below.

$$P = (I_D - A_A)^{-1} \qquad (4)$$

(a) Type A and type B thermal reactions will proceed in a regiochemical manner which maximizes the $\langle DA|\hat{P}|D^+A^-\rangle$ matrix element (HO^D-LU^A type). Under the usual assumption that $H_{ij} = kS_{ij}$,[5] the latter matrix element can be written as follows:

$$\langle DA|\hat{P}|D^+A^-\rangle \propto \langle HO^D|LU^A\rangle \propto c_m{}^{HO}c_n{}^{LU}S_{mn} \qquad (5)$$

In the above expression, $c_m{}^{HO}$ is the coefficient of the π AO of the mth center of the HO of AY, $c_n{}^{LU}$ is the coefficient of an AO of the nth center of the LU of the electrophile, and S_{mn} is the AO overlap integral between the π AO of the mth center of AY and the appropriate AO of the nth center of E$^+$. Accordingly, we say that *the orientation of a thermal electrophilic substitution will be controlled by the HO electron density of the aromatic molecule.*

(b) Photochemical reactions initiated by $\pi\pi^*$ photoexcitation of the aromatic molecule will proceed in a regiochemical

manner which maximizes the $\langle D^*A|\hat{P}|D^+A^-\rangle$ matrix element (LU^D-LU^A type) and simultaneously minimizes the $\langle DA|\hat{P}|D^+A^-\rangle$ matrix element (HO^D-LU^A type). The former interaction matrix element can be written as follows:

$$\langle D^*A|\hat{P}|D^+A^-\rangle \propto \langle LU^D|LU^A\rangle \propto c_m{}^{LU}c_n{}^{LU}S_{mn} \qquad (6)$$

where the various symbols have meaning analogous to that in eq 5. The $\langle DA|\hat{P}|D^+A^-\rangle$ interaction matrix element is given by eq 5. Accordingly, we say that *a photochemical electrophilic substitution will occur in a manner which involves attack of the site of the aromatic molecule having the highest LU electron density and simultaneously the smallest HO electron density.*

(c) As polarity increases, the positional selectivity of type A and type B thermal as well as the positional selectivity of photochemical aromatic electrophilic substitution will decrease.[1] In addition, for a given reactant pair, the positional selectivity of the photochemical reaction will be lower than that of the corresponding thermal reaction.

(d) As polarity increases, the rate of type A and type B thermal aromatic electrophilic substitution will increase.

B. Singlet Nucleophilic Aromatic Substitutions. Proceeding as in the previous case, we can write the following simple reaction scheme for nucleophilic aromatic substitution:

$$AY + N^-M^+ \rightarrow [AY-N]^-M^+ \rightarrow products$$

The zero-order basis set configurations which are necessary for describing the addition step of the reaction sequence shown above along with the associated interaction matrix, are shown in Scheme II, where AY is assumed to be the acceptor A, and

Scheme II. Zero-Order Basis Set Configurations and Interaction Matrix for Nucleophilic Aromatic Substitutions

the nucleophile N$^-$M$^+$ the donor D. The equations of the corresponding diabatic surfaces are given below and the diabatic as well as adiabatic surfaces are similar to those sketched in Figure 1.

$$E(DA) = S(r) \qquad (7)$$

$$E(D^+A^-) = I_D - A_A + S'(r) - C(r) \qquad (8)$$

$$E(DA^*) = G(\pi\pi^*) + S'(r) \qquad (9)$$

The information contained in the adiabatic PE surfaces can be conveyed by chemical equations analogous to the ones given before for electrophilic aromatic substitution. The mechanistic features of the two reaction classes are similar and the regioselection rules are as follows:

(a) Type A and type B thermal reactions will occur in a regiochemical manner which maximizes the $\langle DA|\hat{P}|D^+A^-\rangle$ matrix element (HO^D-LU^A type). The latter matrix element can be written as in eq 5, where $c_n{}^{HO}$ is the coefficient of an AO of the nth center of the HO of the nucleophile and $c_m{}^{LU}$ is the coefficient of an AO of the mth center of the LU of the aromatic molecule. Accordingly, we can say that *the orientation*

of thermal nucleophilic substitution will be controlled by the LU electron density of the aromatic molecule.

(b) The photochemical reaction initiated by $\pi\pi^*$ photoexcitation of the aromatic molecule will proceed in a regiochemical manner which maximizes the $\langle DA^*|\hat{P}|D^+A^-\rangle$ matrix element (HO^D–HO^A type) and simultaneously minimizes the $\langle DA|\hat{P}|D^+A^-\rangle$ matrix element (HO^D–LU^A type). The former matrix element can be written as follows:
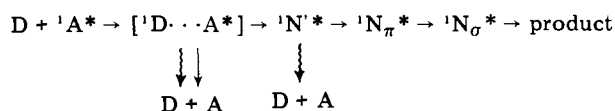
$$\langle DA^*|\hat{P}|D^+A^-\rangle \propto \langle HO^D|LU^D\rangle \propto c_m{}^{HO}c_n{}^{HO}S_{mn} \qquad (10)$$

The various symbols have meanings analogous to those in the previous thermal case. Obviously, the $\langle DA|\hat{P}|D^+A^-\rangle$ matrix element is still given by eq 5. Accordingly, we can say that *a photochemical nucleophilic aromatic substitution will occur in a manner which involves attack of the site of the aromatic molecule having the highest HO electron density, and, simultaneously, the smallest LU electron density.*
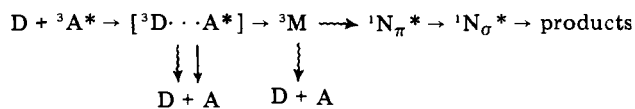
II. Spin–Orbit Coupling and the Regiochemistry of Triplet Photoaromatic Substitutions

In a previous section we discussed the regioselectivity with reference to singlet photoaromatic substitutions. The regioselectivity of the triplet counterparts can be discussed in a similar manner, now using triplet charge transfer and locally excited diabatic surfaces rather than singlet ones. The differences between singlet and triplet photoaromatic substitution can be understood by reference to the chemical equations shown below:

Singlet:

$$D + {}^1A^* \rightarrow [{}^1D\cdots A^*] \rightarrow {}^1N'^* \rightarrow {}^1N_\pi{}^* \rightarrow {}^1N_\sigma{}^* \rightarrow \text{product}$$

$$\downarrow\downarrow \qquad\qquad \downarrow$$

$$D + A \qquad D + A$$

Triplet:

$$D + {}^3A^* \rightarrow [{}^3D\cdots A^*] \rightarrow {}^3M \rightsquigarrow {}^1N_\pi{}^* \rightarrow {}^1N_\sigma{}^* \rightarrow \text{products}$$

$$\downarrow\downarrow \qquad\qquad \downarrow$$
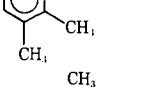
$$D + A \qquad D + A$$

In ionic reactions occurring in solution, solvation effects are known to be important. Thus, the ${}^3M$ intermediate is reasonably expected to be highly solvated in which case the intermolecular contribution to SO coupling can be substantial.[6] In addition, many substituted aromatic molecules are known to have short triplet lifetimes,[7] something which indicates a strong intramolecular contribution to SO coupling. Under these circumstances, it seems reasonable to anticipate that the ${}^3M \rightsquigarrow {}^1N_\pi{}^*$ conversion will be facile, i.e., this will *not* be the rate-determining step in triplet photoaromatic substitutions, at least in most cases. Accordingly, singlet and triplet photoaromatic substitutions may exhibit similar regioselectivity since the regiochemical conditions for optimization of the photochemical barrier are identical for triplet and singlet photoaromatic substitutions.

III. Theory and Experiment

The preceding analysis revealed that triplet and singlet photonucleophilic and photoelectrophilic aromatic substitutions conform to the same regiochemical rules, at least in most cases. Accordingly, in reviewing the experimental data, we shall not be concerned with the multiplicity of the reactive excited state. Exceptional cases when the ${}^3M \rightarrow {}^1N_\pi{}^*$ transformation dictates the regiochemistry of the reaction will be treated separately.[8]
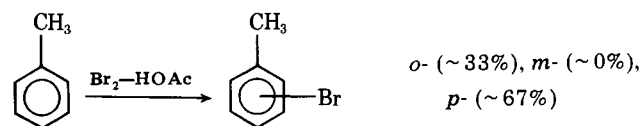
A. Electrophilic Aromatic Substitutions. The preponderance of experimental evidence accumulated as a result of a large number of investigations of electrophilic aromatic substitution are in good accord with our predictions.

Table I. Relative Rates of Bromination and Chlorination of Aromatic Hydrocarbons

Aromatic substrate	IP^a	Relative rate of bromination in 85% HOAc^b	Relative rate of chlorination in 85% HOAc^b
H (benzene)	9.25	1	1
CH₃ (toluene)	8.90	650	340
CH₃, CH₃ (xylene)	8.60	5300	2030
CH₃, CH₃, CH₃	~8.30	1 670 000	30 000 000
CH₃, CH₃, CH₃	~8.00	11 000 000	
CH₃ (hexamethyl)	~7.70	810 000 000	134 000 000

^{a} IP values for benzene, toluene, and *o*-xylene from D. W. Turner, *Adv. Phys. Org. Chem.*, **4**, 30 (1960). The rest of the values were estimated. ^{b} G. A. Olah, *Acc. Chem. Res.*, **4**, 240 (1971).

(a) The regioselectivity of thermal electrophilic aromatic substitution is consistent with the HO electron density control.[9] Typical data are shown below[10] along with CNDO/2 HO electron densities.

o- (~33%), m- (~0%),
p- (~67%)

HO electron density: o-(0.1090), m- (0.0484), p- (0.2805)

(b) The overall rates of thermal electrophilic aromatic substitution reactions can be correlated with the ionization potentials of the aromatic substrates. Typical data are shown in Table I.

(c) The dependence of regioselectivity upon the electronic nature of the reactants follows our predictions. Thus, the data shown in Table II clearly illustrate that as reaction polarity is gradually increased, the para over ortho ratio tends to unity, i.e., *increased polarity leads to reduced regioselectivity.*

A greater challenge is posed by photoelectrophilic aromatic substitution where intuition cannot be used to extrapolate from preexisting data since these reactions have only recently attracted the attention of chemists.
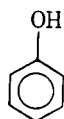
The photodeuteration of anisole is a particularly suitable reaction for illustrating our approach. The ab initio HO electron densities vary in the order *p-* > *o-* > *m-*, while the LU electron densities vary in an exactly opposite manner, i.e., *m-* ≥ *o-* > *p-*, as shown below for phenol as a model substrate.

When such a pattern obtains, an unambiguous prediction can be made. Specifically, we expect that the orientational preference of the photoelectrophilic deuteration of anisole will vary in the order *m-* > *o-* > *p-*, i.e., the order of increasing LU electron density and simultaneously decreasing HO electron density. Experimental results in support of these predictions

Table II. The Dependence of Product Distribution in the Electrophilic Substitution of Toluene on the Nature of the Electrophile

Electrophile	2[para]/[ortho][a]
p-$CH_3OC_6H_4CH_2Cl/TiCl_4$	5.00
p-$CH_3C_6H_4CH_2Cl/TiCl_4$	4.17
p-$HC_6H_4CH_2Cl/TiCl_4$	2.70
p-$ClC_6H_4CH_2Cl/TiCl_4$	2.70
p-$NO_2C_6H_4CH_2Cl/TiCl_4$	1.15
p-$CH_3OC_6H_4SO_2Cl/AlCl_3$	33.30
p-$CH_3C_6H_4SO_2Cl/AlCl_3$	12.50
p-$HC_6H_4SO_2Cl/AlCl_3$	4.35
p-$ClC_6H_4SO_2Cl/AlCl_3$	2.94
p-$NO_2C_6H_4SO_2Cl/AlCl_3$	1.61

[a] G. A. Olah, *Acc. Chem. Res.*, **4**, 240 (1971).

OH

HO electron density: ipso (0.1884), o- (0.1043), m- (0.0426), p- (0.2460)
LU electron density: ipso ($\sim$0), o- (0.3142), m- (0.3320), p- ($\sim$0)

have been reported. Thus, it was found that the product distribution of deuterated anisole is m- (8%), o- (7.5%), and p- (1%).[11] However, dedeuteration results[12] suggest that the product distribution is approximately 6:1:2 for o-, m-, and p-, respectively. Clearly, more experimental work is needed to clarify the situation.

As a second example, we consider the case of photoelectrophilic deuteration of naphthalene. Unlike the case of anisole, the HO and LU electron densities vary in the same direction, i.e., the α position has a higher electron density than the β position in both HO and LU. Accordingly, an unambiguous prediction cannot be made here because simultaneous maximization of the LU^D-LU^A and minimization of the HO^D-LU^A matrix elements is impossible. One has to decide whether traversing the barrier on the excited surface, or crossing from excited to ground state surface, is the rate-determining step. Experimentally, it is found[11] that this reaction exhibits a preference for α-attack. Thus, we are led to hypothesize that photoelectrophilic substitution reactions are barrier-controlled reactions. Hence, we anticipate that *the regioselectivity of photoelectrophilic aromatic substitution will, in general, be controlled by the electron density of the LU of the aromatic molecule.*

B. Nucleophilic Aromatic Substitutions. With respect to thermal nucleophilic aromatic substitution, the following experimental trends conform to our predictions:

(a) The reaction regioselectivity is controlled by the LU electron density of the aromatic substrate.[13]

(b) The overall rate of nucleophilic aromatic substitution can be correlated with the electron affinity of the aromatic substrate. Typical data are shown in Table III.

The mechamism of photonucleophilic aromatic substitutions has attracted considerable interest in recent years.[14-17] As in the case of photoelectrophilic aromatic substitution, we shall examine relevant experimental data in some detail.

As we have stated before, the preferred regioselectivity of photonucleophilic aromatic substitution will be one which simultaneously maximizes the $\langle D^+A^-|\hat{P}|DA^*\rangle$ matrix element and minimizes the $\langle D^+A^-|\hat{P}|DA\rangle$ matrix element. By stating this selection rule we mean that the ideally preferred orientation will be the one which has the lowest photochemical barrier and can undergo the most efficient decay to the ground state. However, this requirement cannot be met in aromatic mole-

Table III. Relative Rates of Nucleophilic Aromatic Substitutions

X	Log k^a
NH_2	-7.6
CH_3	-5.3
H	-4.3
Br	-3.25
$COOCH_3$	-1.44

X	E_a,[b] kcal/mol	Log A
CF_3	31.5	11.0
$COCH_3$	29.2	11.2
NO_2	24	11.2

[a] J. A. Bunnet and R. E. Zahler, *Chem. Rev.*, **49**, 273 (1951). [b] J. Miller and W. K. Yan, *J. Chem. Soc.*, 3494 (1963).

cules where the HO and LU have identical electron density at any given center. This is the case of even alternant hydrocarbons where the pairing theorem holds.[18] As in the case of photoelectrophilic aromatic substitution, we hypothesize that in such cases, the *product distribution is determined by the height of the photochemical barrier, i.e., the HO electron density.*
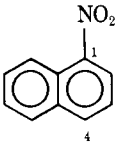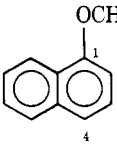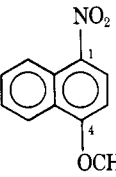
Further complications may arise after decay of the excited complex to ground state N_σ^* complex. At this stage of the reaction, the yield of products will be determined by the leaving group ability. When the leaving group is a "poor" leaving group (e.g., H^-) or there are no appropriate conditions (e.g., an H^- sink) for its abstraction, the N_σ^* complex may decompose back into reactants. This complication may create a situation where the distribution of products will appear to be inconsistent with our theory. This problem does not arise in photoelectrophilic aromatic substitution where H^+ can easily depart.

We now turn to the discussion of two specific experimental cases.

(a) The photosubstitution reaction of anisole provides an intriguing example. In the presence of O_2, which can assist the departure of H^-, nucleophilic attack can occur at the ortho, meta, and para positions. The order of HO electron densities is p- > o- > m- while the order of the LU electron densities is the exact reverse. Accordingly, we can unambiguously predict that the nucleophile will attack the various positions in the following order of increasing preference: p- > o- > m-. This is what is found experimentally.[14] In the absence of O_2, the superiority of MeO^- as a leaving group along with the fact that the ipso position bears a high HO electron density and zero LU electron density dictates preferential nucleophilic attack at C-1.[14]

(b) Alternant hydrocarbons naphthalene and phenanthrene give substitution at the site with the highest HO electron density.[14] These sites are also the sites of highest LU electron density. However, the following data indicate that the photosubstitution is controlled by the HO electron density. Thus, Letsinger et al.[19,20] and Lok et al.[21] reported that 1-nitronaphthalene undergoes nucleophilic substitution at C-1 by CN^-, H^-, and $^-OCH_3$, whereas 1-methoxynaphthalene undergoes substitution by CN^- mainly (98%) at C-4.[22] In addition, 1-nitro-4-methoxynaphthalene undergoes substitution at C-1.[14,23] The difference between the substitution re-

actions of 1-nitronaphthalene and 1-methoxynaphthalene is in full agreement with the substituent effect on the HO electron density. Specifically, NO_2 causes an increase in the coefficient of C-1 and a decrease in the coefficient of C-4, whereas methoxy operates in the opposite direction. This is illustrated by the appropriate extended Hückel HO electron densities:

	NO₂	OCH₃	NO₂ / OCH₃
HO electron density	C-1 (0.060) C-4 (0.036)	C-1 (0.165) C-4 (0.210)	C-1 (0.070) C-4 (0.030)

It should be pointed out that the available experimental data which was compared to the theoretical predictions has to do with *yields* rather than *rates*. The former are not necessarily related to the latter since other deactivation processes, e.g., decay of the encounter complex D···A*, may mask the efforts of barriers and decay funnels. An analysis of the regiochemical dependence of the decay efficiency of D···A* is complicated by the fact that the stability of a weak complex (e.g., D···A, D···A*, etc.) depends on a number of factors.[24] With this in mind, the analysis of the photochemical data is offered as suggestive of a theory–experiment correlation and not as a final proof of the validity of our treatise.[25]

A final cautionary remark: The rules derived in this paper are based on the assumption that the lowest excited state of the aromatic involves HOMO → LUMO excitation. Depending on multiplicity, nature and number of substituents, and structure of the aromatic parent molecule, deviations may occur due to CI effects, i.e., the lowest excited state may involve subHOMO → LUMO and/or HOMO → subLUMO excitations. In such cases, the regioselection rules should be modified appropriately.

References and Notes

(1) See part 1: N. D. Epiotis and S. Shaik, *J. Am. Chem. Soc.*, accompanying paper in this issue.
(2) J. N. Murrell, S. F. Kettle, and J. M. Tedder, "Valence Theory", Wiley, New York, N.Y., 1965, p 334.
(3) The rate of a radiationless decay process increases as the energy gap, ΔQ, becomes smaller. For discussion of this subject see (a) L. Landau, *Phys. Z. Sowjetunion*, **2**, 46 (1932); (b) C. Zener, *Proc. R. Soc. London, Ser. A*, **137**, 696 (1932); (c) G. W. Robinson and R. P. Frosch, *J. Chem. Phys.*, **37**, 1962 (1962); (d) *ibid.*, **38**, 1187 (1963); (e) J. Jortner, *Pure Appl. Chem.*, **27**, 389 (1971).
(4) For interesting discussions of decay processes, see J. Michl, *Fortschr. Chem. Forsch.*, **46**, 1 (1974).
(5) H. C. Longuet-Higgins and M. de V. Roberts, *Proc. R. Soc. London, Ser. A*, **224**, 336 (1954).
(6) Data for solvent effect on phosphorescence lifetime can be found in E. J. Bowen F. R. S., "Luminescence in Chemistry", Van Nostrand, Princeton, N.J., 1968.
(7) S. P. McGlynn, T. Azumi, and M. Kinoshita, "The Triplet State", Prentice-Hall, Englewood Cliffs, N.J., 1969, Chapter 6.
(8) Discussion of selection rules for efficient spin–orbit coupling can be found in part 3 of this series: N. D. Epiotis and S. Shaik, *J. Am. Chem. Soc.*, preceding paper in this issue.
(9) For an earlier treatment of thermal electrophilic aromatic substitutions see K. Fukui, T. Yonezawa, and H. Shingu, *J. Chem. Phys.*, **20**, 722 (1952).
(10) H. C. Brown and L. M. Stock, *J. Am. Chem. Soc.*, **79**, 1421 (1957).
(11) D. A. de Bie and E. Havinga, *Tetrahedron*, **21**, 2359 (1965).
(12) G. Lodder and E. Havinga, *Tetrahedron*, **28**, 5583 (1972).
(13) For earlier treatments of these reactions see (a) K. Fukui, T. Yonezawa, C. Nagata, and H. Shingu, *J. Chem. Phys.*, **22**, 1433 (1954); (b) N. D. Epiotis, *J. Am. Chem. Soc.*, **95**, 3188 (1973).
(14) J. Cornelisse and E. Havinga, *Chem. Rev.*, **75**, 353 (1975).
(15) J. Cornelisse, *Pure Appl. Chem.*, **41**, 433 (1975).
(16) J. Cornelisse, G. P. De Gunst, and E. Havinga, *Adv. Phys. Org. Chem.*, **11**, 225 (1975).
(17) E. Havinga and J. Cornelisse, *Pure Appl. Chem.*, **47**, 1 (1976).
(18) See discussion in W. T. Borden, "Modern Molecular Orbital Theory for Organic Chemistry", Prentice-Hall, Englewood Cliffs, N.J., 1975, p 86.
(19) R. L. Letsinger and R. R. Hautala, *Tetrahedron Lett.*, 4205 (1969).
(20) W. C. Petersen and R. L. Letsinger, *Tetrahedron Lett.*, 2197 (1971).
(21) C. M. Lok, J. Lugtenburg, J. Cornelisse, and E. Havinga, *Tetrahedron Lett.*, 4701 (1970).
(22) C. M. Lok and E. Havinga, *Proc. K. Ned. Akad. Wet., Ser. B*, **77**, 15 (1974).
(23) C. M. Lok, Thesis, University of Leiden, Leiden, 1972.
(24) For example, see H. Umeyama and K. Morokuma, *J. Am. Chem. Soc.* **98**, 7208 (1976), and previous papers.
(25) Charge iterative extended Huckel calculations were performed using a program kindly provided by Professor E. R. Davidson. For the original work, see R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963). The CNDO/2 computations were carried out using the program described in J. A. Pople and D. L. Beveridge, "Approximate Molecular Orbital Theory", McGraw-Hill, New York, N.Y., 1970. The ab initio computations, using an STO-3G basis set, were carried out using the Gaussian 70 series of programs (W. J. Hehre, W. A. Lathan, R. Ditchfield, M. D. Newton, and J. A. Pople, Quantum Chemistry Program Exchange, University of Indiana, Bloomington, Ind.) by Professor F. Bernardi of the University of Bologna.

The Electronic Structure of the Low-Lying Excited States of Glyoxal

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Abstract: We have studied the electronic structure of the low-lying states of glyoxal, in particular the two lowest triplets ^3A_u (n → π*) and ^3B_u (π → π*). We find that the SCF predicted order of energies ($^3B_u < {}^3A_u$) is reversed in a configuration interaction calculation.

Introduction

Glyoxal is the simplest of the α-dicarbonyl compounds and has been of interest to photochemists and spectroscopists for at least half a century. In this time a great deal of effort has been directed toward the identification of photoproducts and the excited electronic states from which they originate.[1,2] The consensus in the literature is that the reactive triplet state in the gas phase is the ^3A_u (n–π*) state with the possibility of a "hot" ground state being responsible for some product formation.[2] Because of Kasha's rules[3] it has been assumed that this ^3A_u state is the lowest triplet.