(12) (a) K. Ruedenberg, *Rev. Mod. Phys.*, **34**, 326 (1962); (b) R. R. Rue and K. Ruedenberg, *J. Phys. Chem.*, **68**, 1676 (1964); (c) C. Edmiston and K. Ruedenberg, *ibid.*, **68**, 1628 (1964).
(13) M. S. Gordon, D. E. Tallman, C. Monroe, M. Steinbach, and J. Armbrust, *J. Am. Chem. Soc.*, **97**, 1326 (1975).
(14) J. A. Pople, D. L. Beveridge, and P. A. Dobosh, *J. Chem. Phys.*, **47**, 2026 (1967).
(15) (a) A. Pullman, *Int. J. Quantum Chem., Symp.*, **No. 2**, 187 (1968); (b) C. Giessner-Prettre, and A. Pullman, *Theor. Chim. Acta*, **13**, 765 (1969); (c) J. Del Bene and H. H. Jaffe, *J. Chem. Phys.*, **48**, 1807 (1968).
(16) P. M. Saatzer, R. D. Koob, and M. S. Gordon, "Excited States and Photochemistry of Saturated Molecules. II. Optimal Geometries in a Number of Low-Lying States of Propane", in preparation.
(17) P. M. Saatzer and M. S. Gordon, "The Effect of Ground State Geometry on the Order of Vertical Excited States and Orbital Ordering. CNDO vs. INDO", in preparation.
(18) J. A. Pople and M. S. Gordon, *J. Am. Chem. Soc.*, **89**, 4253 (1967).
(19) J. Jortner, S. A. Rice, and R. M. Hochstrasser, *Adv. Photochem.*, **7**, 149 (1969).
(20) J. H. Vorachek and R. D. Koob, *Can. J. Chem.*, **51**, 344 (1973). This simplified representation does not include the numerous fragments which may result from subsequent dissociation (or the indistinguishable two-bond primary fragmentation yielding one molecule and two radicals). This aspect is discussed in this citation and ref 4a. Both contain numerous references to earlier work.
(21) D. W. L. Griffiths and R. A. Back, *J. Chem. Phys.*, **46**, 3913 (1967).
(22) At least 95% of propane's photodecomposition involves an H atom. Whenever a state predicts a weak C–C bond, a C–H bond differs in energy by less than $\frac{1}{3}$ eV. Contrast this to states $1B_2$ and $2A_1$ where the secondary C–H bonds are 0.63 eV weaker than C–C.

Calculations of the Magnetic Moments of Some Benzene Derivatives

Akira Kaito, Akio Tajiri, and Masahiro Hatano*

Contribution from the Chemical Research Institute of Non-Aqueous Solutions, Tohoku University, Sendai 980, Japan. *Received October 11, 1974*

Abstract: We have calculated the magnetic moments in the $^1E_{1u}$ and $^1E'$ states of various benzene derivatives with D_{6h}, D_{3h}, and C_{3h} symmetries using wave functions obtained from the Pariser–Parr–Pople (PPP) method. For the benzene derivatives containing electron-donating substituents, the calculated magnetic moments are in good agreement with the experimental values obtained from our previous MCD measurements both in sign and in magnitude. The magnitudes of the calculated magnetic moments of benzene derivatives having electron accepting substituents are much smaller than those of benzene derivatives containing electron-donating groups, which is consistent with the experimental results that the benzene derivatives with strong electron-accepting functions showed no magnetic circular dichroism for the $^1E' \leftarrow {}^1A_1'$ and $^1E' \leftarrow {}^1A'$ transitions.

The magnetic circular dichroism (MCD) technique has thus far been tested by many authors aiming at making it possible to elucidate complicated electronic spectra and magnetic properties of ions and molecules in their ground and excited electronic states.[1-3] Of much interest in recent MCD work, benzene and its derivatives have been studied because of their intriguing spectral features in their longer wavelength spectral region.[4-10] The vibrational structure observed in the MCD spectrum of the $^1B_{2u} \leftarrow {}^1A_{1g}$ transition of benzene itself was analyzed in detail by Shieh,[6] Caldwell,[7] and Douglas[9] and also the effects of substitutions on the sign and magnitude of MCD spectra of the $^1B_{2u} \leftarrow {}^1A_{1g}$ and $^1B_{1u} \leftarrow {}^1A_{1g}$ transitions were investigated.[5,7,8,10] On the other hand, the magnetic circular dichroism of various nonbenzenoid aromatic hydrocarbons[11-13] has also been investigated in our laboratory. In this work, the Faraday *A* term, which should be expected when either the ground or excited state of a compound is degenerate, was studied and the magnetic moments of degenerate excited states of nonbenzenoid aromatic hydrocarbons were extracted. These values were in good agreement with those calculated using wave functions obtained from PPP and CNDO procedures.[13,14]

It seems also interesting to investigate magnetic circular dichroism of the $^1E_{1u} \leftarrow {}^1A_{1g}$ transitions of benzene derivatives and to obtain the magnetic moments in the $^1E_{1u}$ states. We have already reported the MCD spectra of some benzene derivatives[15,16] with D_{6h}, D_{3h}, and C_{3h} symmetries. The $^1E_{1u} \leftarrow {}^1A_{1g}$ transition of benzene corresponds to the $^1E' \leftarrow {}^1A_1'$ and $^1E' \leftarrow {}^1A'$ transitions in D_{3h} and C_{3h} symmetries, respectively. In the region of these transitions, halogenobenzenes, phloroglucin, 1,3,5-trimethoxybenzene, and 1,3,5-tricyanobenzene showed Faraday *A* terms. From the observed MCD and uv spectra, *A*/*D* values were extracted by use of the method of moments[2] together with *B*/*D* values, and these values are shown in Table I. However, 1,3,5-trinitrobenzene, 1,3,5-benzenetricarboxylic acid, and 1,3,5-benzenetricarbonyl chloride indicated no magnetic circular dichroism for these electronic transitions and the magnetic moments in the $^1E'$ states of these molecules seem to be quenched.

It is the purpose of this paper to calculate the magnetic moments in the $^1E_{1u}$ and $^1E'$ states of these benzene derivatives using wave functions obtained from the Pariser–Parr–Pople (PPP) method[17-19] and to explain the experimental results from our previous MCD measurements[15,16] of benzene derivatives.

Calculations of Magnetic Moments

We have calculated the magnetic moments in the $^1E_{1u}$ and $^1E'$ states of benzene derivatives using wave functions determined on the basis of the PPP method including configuration interaction (CI). One-center core and repulsion integrals were evaluated from valence state ionization potentials and electron affinities. Two-center core and repulsion integrals were calculated by use of the Wolfsberg–Helmholtz[20] and Nishimoto–Mataga[21] equations, respectively. For the methoxyl group (OCH_3), we took account of the effect of hyperconjugation using the method offered by Lindner and Mårtensson.[22] We have calculated the electronic transition energies of benzene derivatives and show them in Table II along with the experimental values. The calculated values are in good agreement with the experimental data.

If we use real wave functions, the magnetic moments, μ, in the $^1E_{1u}$ and $^1E'$ states of benzene derivatives are ex-

Table I. Extracted Faraday Parameters for the $^1E_{1u} \leftarrow {}^1A_{1g}$, $^1E' \leftarrow {}^1A_1'$, and $^1E' \leftarrow {}^1A'$ Transitions of Benzene Derivatives with D_{6h}, D_{3h}, and C_{3h} Symmetries, Respectively

Compd	A/D, β	B/D, β/cm^{-1}
Hexachlorobenzene	0.182	-1.98×10^{-5}
Hexabromobenzene	0.207	-4.45×10^{-5}
1,3,5-Trichlorobenzene	0.323	-5.79×10^{-5}
1,3,5-Tribromobenzene	0.301	-7.54×10^{-5}
Phloroglucin	0.127	-1.29×10^{-5}
1,3,5-Trimethoxybenzene	0.262	2.49×10^{-5}
1,3,5-Tricyanobenzene	0.172	-2.35×10^{-5}

Table II. Observed and Calculated Transition Energies

Compd	ν_{obsd}, eV	ν_{calcd}, eV	Compd	ν_{obsd}, eV	ν_{calcd}, eV
Hexachloro-		4.21	1,3,5-Tricyano-	4.34	4.41
benzene	5.34	5.07	benzene	5.45	5.39
	5.71	5.79		5.81	5.74
Hexabromo-		4.21	1,3,5-Trinitro-	3.75[a]	
benzene	4.94	5.02	benzene	4.28	4.26
	5.43	5.68		5.06	5.08
				5.61	5.30
1,3,5-Trichloro-	4.54	4.53			
benzene	5.60	5.58	1,3,5-Benzenetri-	4.39	4.39
	6.18	6.17	carboxylic	5.35	5.28
			acid	5.85	5.62
1,3,5-Tribromo-	4.50	4.51			
benzene	5.52	5.51	1,3,5-Benzenetri-	4.26	4.39
	5.88	6.02	carbonyl	5.06	5.28
			chloride	5.47	5.64
Phloroglucin	4.63	4.42			
	5.64	5.55	Benzene	4.89[b]	4.91
	6.12	6.18		6.17[b]	6.20
				6.98[b]	7.03
1,3,5-Tri-	4.68	4.40			
methoxy-	5.46	5.49			
benzene	6.04	6.10			

[a] $n \rightarrow \pi^*$ transition of nitro group. [b] K. Kimura and S. Nagakura, *Mol. Phys.*, 9, 117 (1965).

pressed as $-(i\beta/\hbar)\langle {}^1E_{1ux}|L_z|{}^1E_{1uy}\rangle$ and $-(i\beta/\hbar)\langle {}^1E'_x|L_z|{}^1E'_y\rangle$, respectively, where L_z is the total electronic orbital angular momentum operator and β is the Bohr magneton. The electronic states, $|{}^1E_{1ux}\rangle$, $|{}^1E_{1uy}\rangle$, $|{}^1E'_x\rangle$, and $|{}^1E'_y\rangle$ are expressed as linear combinations of singly excited configurations. The calculation of magnetic moments in the excited electronic states reduces to the calculation of the matrix element $\langle\Phi(i \rightarrow j)|L_z|\Phi(k \rightarrow l)\rangle$, where $\Phi(i \rightarrow j)$ represents a configuration where one electron is excited from the ith molecular orbital, ϕ_i, to the jth molecular orbital, ϕ_j. If $i \neq k$ and $j \neq l$, $\langle\Phi(i \rightarrow j)|L_z|\Phi(k \rightarrow l)\rangle$ equals zero because of the orthogonality of the molecular orbitals, and if $i = k$ and $j = l$, $\langle\Phi(i \rightarrow j)|L_z|\Phi(k \rightarrow l)\rangle$ becomes zero unless L_z belongs to the totally symmetric representation. If $i = k$ and $j \neq l$,

$$\langle\Phi(i \rightarrow j)|L_z|\Phi(k \rightarrow l)\rangle = \langle\phi_j|l_z|\phi_l\rangle \tag{1}$$

and if $i \neq k$ and $j = l$,

$$\langle\Phi(i \rightarrow j)|L_z|\Phi(k \rightarrow l)\rangle = \langle\phi_i|l_z|\phi_k\rangle \tag{2}$$

where l_z is the one-electron angular momentum operator,

$$l_z = -i\hbar\{X(\partial/\partial Y) - Y(\partial/\partial X)\} \tag{3}$$

In the LCAO-MO approximation, the matrix elements $\langle\phi_i|l_z|\phi_k\rangle$ can be expanded into those between atomic orbitals. Therefore, one obtains

$$\langle\phi_i|l_z|\phi_k\rangle = \sum_a\sum_b C_{ia}C_{kb}\langle\chi^\lambda{}_a|l_z|\chi^\lambda{}_b\rangle \tag{4}$$

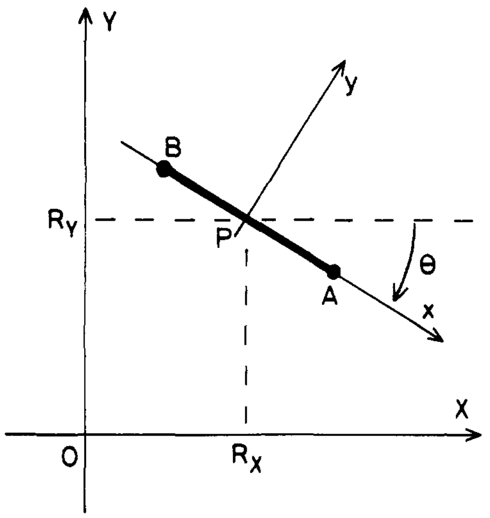


Figure 1. An origin transformation of l_z from O to P.

where the molecular orbital ϕ_i is represented as eq 5, using atomic orbitals $\chi^\lambda{}_a$.

$$\phi_i = \sum_a C_{ia}\chi^\lambda{}_a \tag{5}$$

As differential overlap is neglected in the PPP method, we should consider $\chi^\lambda{}_a$ in eq 4 to be Löwdin orbitals.[23] A set of Löwdin orbitals, χ^λ, can be expressed by that of Slater orbitals, χ^s, as

$$\chi^\lambda = \chi^s S^{-1/2} \tag{6}$$

where S is the overlap matrix calculated by use of Slater $2p_z$ AO's. From eq 6, the following relation is obtained

$$\boldsymbol{l}_z^\lambda = S^{-1/2}\boldsymbol{l}_z^s S^{-1/2} \tag{7}$$

where $\boldsymbol{l}_z^\lambda$ and $\boldsymbol{l}_z^s$ are the matrices of the angular momentum operator calculated using Löwdin orbitals and Slater $2p_z$ AO's, respectively.

Let us consider the calculation of the elements of $\langle\chi^s{}_a|l_z|\chi^s{}_b\rangle$. If the origin for l_z is transferred from the center of gravity of the molecule, O, to the middle point between the A and B atoms, P, and then this coordinate system is rotated by θ in the x–y plane so that the direction of the x axis coincides with a bond between the A and B atoms as shown in Figure 1, one obtains

$$l_z = -i\hbar[\{x(\partial/\partial y) - y(\partial/\partial x)\} + (R_X\cos\theta - R_Y\sin\theta)(\partial/\partial y) - (R_Y\cos\theta + R_X\sin\theta)(\partial/\partial x)] \tag{8}$$

where R_X and R_Y are the X and Y components of the line joining the center of gravity of the molecule, O, and the middle point between the A and B atoms, P. Since $\langle\chi^s{}_a|\partial/\partial y|\chi^s{}_b\rangle = 0$ and $\langle\chi^s{}_a|x(\partial/\partial y) - y(\partial/\partial x)|\chi^s{}_b\rangle = 0$, eq 8 becomes

$$\langle\chi^s{}_a|l_z|\chi^s{}_b\rangle = i\hbar(R_Y\cos\theta + R_X\sin\theta)\langle\chi^s{}_a|\partial/\partial x|\chi^s{}_b\rangle \tag{9}$$

The expressions for $\langle\chi^s{}_a|\partial/\partial x|\chi^s{}_b\rangle$ are given in the appendix of the paper[24] by Imamura. The effective nuclear charge, Z_{eff}, and effective quantum number, n_{eff}, of a Slater orbital were calculated by Slater's rule.[25]

All the calculations were performed by a NEAC 2200 computer in the computer center of Tohoku University.

Results and Discussion

The calculated and observed magnetic moments in the $^1E_{1u}$ and $^1E'$ states are shown in Table III. Halogen atoms and hydroxyl and methoxyl groups are electron-donating

Table III. Observed and Calculated Magnetic Moments in the $^1E_{1u}$ and $^1E'$ States of Benzene Derivatives

Compd	μ_{obsd}, β	$\mu_{calcd,1}$,[a] β	$\mu_{calcd,2}$,[b] β
Hexachlorobenzene	−0.363	−0.470	−0.448
Hexabromobenzene	−0.413	−0.495	−0.478
1,3,5-Trichlorobenzene	−0.646	−0.452	−0.459
1,3,5-Tribromobenzene	−0.603	−0.486	−0.533
Phloroglucin	−0.254	−0.459	−0.426
1,3,5-Trimethoxybenzene	−0.523	−0.457	−0.435
1,3,5-Tricyanobenzene	−0.344	−0.036	−0.095
1,3,5-Trinitrobenzene		0.208	0.058
1,3,5-Benzenetricarboxylic acid		−0.115	−0.198
1,3,5-Benzenetricarbonyl chloride		0.031	−0.113
Benzene		−0.264	−0.264

[a] Calculated including full configuration interaction between singly excited configurations. [b] Calculated including partial configuration interaction between singly excited configurations.

Table IV. Calculated Orbital Angular Momenta and Magnetic Moments in the $^1E_{1u}$ and $^1E'$ States of Benzene Derivatives

Compd	$\langle\phi_\xi\|l_z\|\phi_\eta\rangle$ ($\hbar/i$)	$\langle\phi_x\|l_z\|\phi_y\rangle$ ($\hbar/i$)	$\mu_{calcd,2}$, β
Hexachlorobenzene	0.965	0.517	−0.448
Hexabromobenzene	0.972	0.493	−0.478
1,3,5-Trichlorobenzene	0.991	0.532	−0.459
1,3,5-Tribromobenzene	0.994	0.462	−0.533
Phloroglucin	0.952	0.526	−0.426
1,3,5-Trimethoxybenzene	0.962	0.527	−0.435
1,3,5-Tricyanobenzene	0.731	0.636	−0.095
1,3,5-Trinitrobenzene	0.509	0.566	0.058
1,3,5-Benzenetricarboxylic acid	0.729	0.531	−0.198
1,3,5-Benzenetricarbonyl chloride	0.693	0.580	−0.113
Benzene	1.064	0.800	−0.264

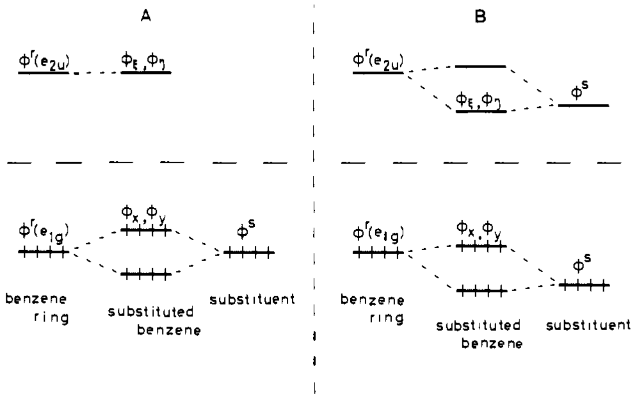


Figure 2. Interaction of the highest occupied and the lowest vacant molecular orbitals of the benzene ring with the electron donating (A) and electron accepting (B) substituent orbitals.

groups, and cyano, nitro, and carbonyl groups are electron-accepting ones. For the benzene derivatives with electron-donating substituents, the calculated magnetic moments are in good agreement with the experimental values both in sign and in magnitude. The magnitudes of the calculated magnetic moments of benzene derivatives with electron accepting groups are much smaller than those of benzene derivatives with electron-donating substituents, which well explains the experimental results that 1,3,5-trinitrobenzene, 1,3,5-benzenetricarboxylic acid, and 1,3,5-benzenetricarbonyl chloride indicated no magnetic circular dichroism in the region of the $^1E' \leftarrow {}^1A_1'$ and $^1E' \leftarrow {}^1A'$ transitions.

Including partial configuration interaction, the $^1E_{1u}$ states of benzene derivatives with D_{6h} symmetry are written as follows

$$|^1E_{1ux}\rangle = (\tfrac{1}{2})[|\phi_y\bar{\phi}_y\phi_x\bar{\phi}_\xi| + |\phi_y\bar{\phi}_y\phi_\xi\bar{\phi}_x| + |\phi_y\bar{\phi}_\eta\phi_x\bar{\phi}_x| + |\phi_\eta\bar{\phi}_y\phi_x\bar{\phi}_x|] \quad (10)$$

$$|^1E_{1uy}\rangle = (\tfrac{1}{2})[|\phi_y\bar{\phi}_y\phi_x\bar{\phi}_\eta| + |\phi_y\bar{\phi}_y\phi_\eta\bar{\phi}_x| - |\phi_y\bar{\phi}_\xi\phi_x\bar{\phi}_x| - |\phi_\xi\bar{\phi}_y\phi_x\bar{\phi}_x|] \quad (11)$$

where ϕ_x, ϕ_y, ϕ_ξ, and ϕ_η denote the highest occupied and the lowest vacant MO's and transform like X, Y, $(X^2 - Y^2)/2$, and XY, respectively. Then, the magnetic moments in the $^1E_{1u}$ states are

$$\mu = -(i\beta/\hbar)[\langle\phi_\xi|l_z|\phi_\eta\rangle - \langle\phi_x|l_z|\phi_y\rangle] \quad (12)$$

For the molecules with D_{3h} and C_{3h} symmetries, eq 12 can be derived similarly. The values calculated from eq 12 are shown in the last column of Table III. These values are not so different from those calculated including full configuration interaction which are shown in the middle column of Table III. Therefore, the effects of configuration interaction are considered to be small in the present cases.

The calculated values of orbital angular momentum $\langle\phi_\xi|l_z|\phi_\eta\rangle$ and $\langle\phi_x|l_z|\phi_y\rangle$ and the magnetic moment, μ, are listed in Table IV. In the cases of benzene derivatives with electron-donating groups, the substituent orbitals more strongly interact with the highest occupied orbitals than the lowest vacant orbitals of the benzene ring, which is shown in Figure 2. Therefore, the magnitude of $\langle\phi_x|l_z|\phi_y\rangle$ decreased more than that of $\langle\phi_\xi|l_z|\phi_\eta\rangle$, resulting in the increase of the magnetic moments, μ, in the $^1E_{1u}$ and $^1E'$ states of benzene derivatives with electron-donating substituents. On the other hand, Figure 2 indicates that the molecular orbitals of electron-accepting groups are preferentially mixed with the lowest vacant orbitals rather than the highest occupied orbitals of the benzene ring, and the magnitude of $\langle\phi_\xi|l_z|\phi_\eta\rangle$ decreased more than that of $\langle\phi_x|l_z|\phi_y\rangle$, leading to the decrease of the magnetic moments in the $^1E_{1u}$ and $^1E'$ states of benzene derivatives with electron-accepting groups.

Our calculations of the magnetic moments clearly explain most of the experimental results from our previous MCD measurements.[15,16] However, the magnetic moment calculated for 1,3,5-tricyanobenzene is smaller than that obtained from the MCD and uv spectra. Probably, this discrepancy arises from the choice of the semiempirical parameters of the PPP method and the effective nuclear charges. The magnitudes of the experimental magnetic moments of hexahalogenated benzenes are smaller than those of 1,3,5-trihalogenated benzenes, which cannot be explained by our calculations. This inconsistency may be based on the fact that we have used the same structural and semiempirical parameters for the calculations of the magnetic moments of hexa- and 1,3,5-trihalogenated benzenes.

As shown in Table I, the contributions of the Faraday *B* terms to the MCD bands of $^1E_{1u} \leftarrow {}^1A_{1g}$, $^1E' \leftarrow {}^1A_1'$, and $^1E' \leftarrow {}^1A'$ transitions cannot be neglected. In D_{6h} symmetry, these Faraday *B* terms are considered to be caused by the mixing of the wave functions of the $^1E_{1u}$ states with those of the other higher $^1E_{1u}$ states and also the vibronic states, $|^1B_{2u}, e_{2g}\rangle$ and $|^1B_{1u}, e_{2g}\rangle$, where $|^1B_{2u}, e_{2g}\rangle$ and $|^1B_{1u}, e_{2g}>$ mean that one quantum of e_{2g} vibrational mode is excited in the $^1B_{2u}$ and $^1B_{1u}$ states, respectively. The same explanation can be applied to the cases of D_{3h} and C_{3h} symmetries.

Conclusion

The magnetic moments in the $^1E_{1u}$ and $^1E'$ states of benzene derivatives were calculated by use of wave functions obtained from the PPP method. The calculated values are in good agreement with those derived from MCD and uv spectra.[15,16] Our calculations suggest that the magnetic moments in the $^1E_{1u}$ and $^1E'$ states of benzene derivatives are increased by the substitutions of electron-donating functions and are quenched by the effects of electron-accepting substituents, which is consistent with the experimental data. It may be concluded that the PPP method is available for the calculations of the magnetic moments of aromatic molecules. An unsatisfactory result for 1,3,5-tricyanobenzene may arise from the choice of the semiempirical parameters of the PPP method and the effective nuclear charges, or the scheme determining the wave functions in the excited electronic states.

References and Notes

(1) A. D. Buckingham and P. J. Stephens, *Annu. Rev. Phys. Chem.*, **17**, 399 (1966).

(2) P. N. Schatz and A. J. McCaffery, *Q. Rev. Chem. Soc.*, **23**, 552 (1969).

(3) D. Caldwell, J. M. Thorne, and H. Eyring, *Annu. Rev. Phys. Chem.*, **22**, 259 (1971).

(4) P. J. Stephens, P. N. Schatz, A. B. Ritchie, and A. J. McCaffery, *J. Chem. Phys.*, **48**, 132 (1968).

(5) J. G. Foss and M. E. McCarville, *J. Am. Chem. Soc.*, **89**, 30 (1967).

(6) D. J. Shieh, S. H. Lin, and H. Eyring, *Proc. Natl. Acad. Sci. U.S.*, **69**, 2000 (1972).

(7) D. J. Caldwell and H. Eyring, *J. Chem. Phys.*, **58**, 1149 (1973).

(8) D. J. Shieh, S. H. Lin, and H. Eyring, *J. Phys. Chem.*, **77**, 1031 (1973).

(9) I. N. Douglas, R. Grinter, and A. J. Thomson, *Mol. Phys.*, **26**, 1257 (1973).

(10) D. W. Miles and H. Eyring, *Proc. Natl. Acad. Sci. U.S.*, **70**, 3754 (1973).

(11) A. Tajiri and M. Hatano, *Bull. Chem. Soc. Jpn.*, **45**, 962 (1972).

(12) H. Uchimura, A. Tajiri, and M. Hatano, *Chem. Phys. Lett.*, **19**, 513 (1973).

(13) A. Tajiri and M. Hatano, *Chem. Phys. Lett.*, **25**, 546 (1974).

(14) A. Tajiri, H. Uchimura, and M. Hatano, *Chem. Phys. Lett.*, **21**, 568 (1973).

(15) A. Kaito, A. Tajiri, and M. Hatano, *Chem. Phys. Lett.*, **25**, 548 (1974).

(16) A. Kaito, A. Tajiri, and M. Hatano, *Chem. Phys. Lett.*, **28**, 197 (1974).

(17) R. Pariser and R. G. Parr, *J. Chem. Phys.*, **21**, 466 (1953).

(18) R. Pariser and R. G. Parr, *J. Chem. Phys.*, **21**, 767 (1953).

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

(20) M. Wolfsberg and L. Helmholtz, *J. Chem. Phys.*, **20**, 837 (1952).

(21) N. Mataga and K. Nishimoto, *Z. Phys. Chem.* (*Frankfurt am Main*), **12**, 335 (1957).

(22) P. Lindner and O. Mårtensson, *Theor. Chim. Acta*, **7**, 352 (1967).

(23) P. O. Löwdin, *J. Chem. Phys.*, **18**, 365 (1950).

(24) A. Imamura, T. Hirano, C. Nagata, and T. Tsuruta, *Bull. Chem. Soc. Jpn.*, **45**, 396 (1972).

(25) J. C. Slater, *Phys. Rev.*, **36**, 57 (1930).

Diffusion Model Analysis of Cage Reactions of Chiral Radical Pairs

John F. Garst[1]

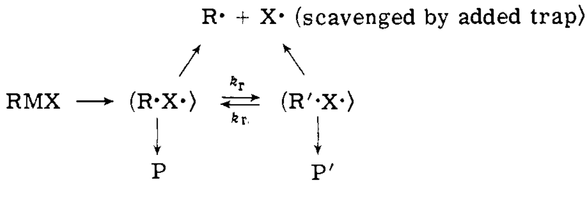
Contribution from the Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, and the Department of Chemistry, The University of Georgia, Athens, Georgia 30602.

Received March 10, 1975

Abstract: The diffusion radical pair model of Noyes is used in the analysis of data on the extent of racemization accompanying formation of cage coupling products in decompositions of radical pair precursors RMX, where R is the chiral group 1-phenylethyl, M is a small molecule extruded in the decomposition, and X is another group. It is found that the fraction s of retention of configuration (vs. racemization) in the coupling product is $e^{-2(a/\tau_r)^{1/2}}$, where a is a parameter dependent on the reactivity and diffusion characteristics of the radicals and τ_r is the rotational relaxation time of R·. There is excellent agreement between τ_r estimated on this basis from experimental data and τ_r estimated from dielectric relaxation experiments on ethylbenzene, a model for R·. Experiments involving decompositions of RMR can, in principle, serve to distinguish the diffusion model from a much simpler model in which radical pair recombination and diffusive separation are taken to be first-order processes. Unfortunately, when $D\tau_r$ is in its usual range (D = relative diffusion coefficient of the radicals), the method is not likely to succeed because of insufficient differences between the predictions of the two models. The treatment of this problem is closely related to that of the encroachment of scavengers on secondary geminate recombination, for which an equation, obtained by Noyes in the form of a truncated series, is given.

Reactive free radicals generated as pairs in solution may react with one another before diffusing apart or reacting with scavengers which may be present. Relevant to such "cage reactions"[2,3] or "geminate recombinations"[4] there exists a substantial body of theory and experiment.[2]

Data have been obtained recently for several cases in which the cage reactions compete with the racemization of initially chiral radical pairs (eq 1).[5-7] In RMX, R is a chiral



(1)

group (1-phenylethyl in the cases so far studied), M is a small molecule extruded in the thermal decomposition (e.g., nitrogen or carbon dioxide), and X is another group (in one case studied, X = R). (R′·X·) is a radical pair in which the radical R· has rotated to expose to X· the face opposite that through which it was originally bound; (R·X·) and (R′·X·) are enantiomeric radical pairs which collapse to give products P and P′, respectively. The rotation of R· is a first-order process governed by the rate constant k_r or the relaxation time $\tau_r = 1/2k_r$. Radical pairs which suffer separation by diffusion are scavenged by a radical trap which is present, so that P and P′ are formed only in cage reactions. Experimentally, the cage yield b and the fraction s of retention of configuration (the remainder being racemization) in the combination products RX are determined. In Table I are collected experimental values of b and s.

The data were treated originally in terms of a "first-order" model in which radical pair reaction and diffusive separation are governed by first-order rate constants k_c (cage reaction) and k_d (diffusive separation).[5-7] However,