Electronic Interactions between Molecules and Atoms (Radicals) Involving Excited States

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A number of reactions can be discussed from the standpoint of the potential-energy surface[1]. The chemical reactivity of conjugated molecules for a radical attack can sometimes be interpreted in terms of the enegy change of the ground state of the system arising from the radical attack[2]. The quenching of excited (^{2}P) sodium by a molecule is interpreted on the basis of the potential-energy surfaces[3] of the system, involving the excited state of the sodium

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[1] S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes", McGraw-Hill Book Co., Inc., New York (1941).

[2] R. D. Brown, *J. chim. phys.*, **50**, 109 (1953).

[3] K. J. Laidler, "Chemical Kinetics of Excited States", Oxford University Press, London (1955).

atom. In the present paper the chemical reactivity of conjugated molecules and the quenching of excited sodium will be discussed on the basis of the electronic structures of the molecules by giving the energy change for a radical attack or the potential-energy surfaces of the system. The importance of the lowest triplet states of molecules in their chemical reactivity to a radical attack, in addition to the role of the electron-transfer states in the quenching of excited sodium, will be discussed.

In previous papers[4,5], the present author has given a theoretical interpretation of the electronic spectrum of the benzyl radical under the assumption that the benzyl radical is composed of a benzene ring and a methylene radical. Since the electronic system, composed of an atom (or a radical) and a molecule, is similar to that of the benzyl radical, a theoretical treatment similar to those of the previous papers will be undertaken in the present work.

Wave Functions

The configurational wave functions of the whole system can be written as follows:

a) Doublet states ($M_S=+1/2$)

$$\Psi_0=\phi_0\cdot\chi_0^\alpha$$

$$\Psi_S(i-l)=\phi_s(i-l)\cdot\chi_0^\alpha$$

$$\Psi_T^{\frac{1}{2}}(i-l)=1/\sqrt{3}\{\phi_t^0(i-l)\cdot\chi_0^\alpha -\sqrt{2}\phi_t^1(i-l)\cdot\chi_0^\beta\}$$

$$\Psi_X=\phi_0\cdot\chi_1^\alpha$$

$$\Psi_C(i-\chi_0)=(1^\alpha 1^\beta\cdots\cdots i^\alpha\cdots\cdots n^\alpha n^\beta \chi_0^\alpha \chi_0^\beta)$$

$$\Psi_C(\chi_0-l)=(1^\alpha 1^\beta\cdots\cdots n^\alpha n^\beta l^\alpha)$$

b) Quartet states ($M_S=+3/2$)

$$\Psi_T^{\frac{3}{2}}(i-l)=\phi_t^1(i-l)\cdot\chi_0^\alpha$$

where $\phi_s(i-l)$, $\phi_t^0(i-l)$ and $\phi_t^1(i-l)$ are the wave functions of the excited states of the molecule, in which one electron has been excited from an occupied MO (i) to a vacant MO (l).

$$\phi_0=(1^\alpha 1^\beta\cdots\cdots i^\alpha i^\alpha\cdots\cdots n^\alpha n^\beta)$$

$$\phi_s(i-l)=1/\sqrt{2}\{(1^\alpha 1^\beta\cdots\cdots i^\alpha l^\beta\cdots\cdots n^\alpha n^\beta) -(1^\alpha 1^\beta\cdots\cdots i^\beta l^\alpha\cdots\cdots n^\alpha n^\beta)\}$$

$$\phi_t^0(i-l)=1/\sqrt{2}\{(1^\alpha 1^\beta\cdots\cdots i^\alpha l^\beta\cdots\cdots n^\alpha n^\beta) +(1^\alpha 1^\beta\cdots\cdots i^\beta l^\alpha\cdots\cdots n^\alpha n^\beta)\}$$

$$\phi_t^1(i-l)=(1^\alpha 1^\beta\cdots\cdots i^\alpha l^\alpha\cdots\cdots n^\alpha n^\beta)$$

The abbreviations are as follows:

i: an occupied MO of the molecule
l: a vacant MO of the molecule
χ_0: the singly occupied orbital in the ground state of the atom (or the radical)
χ_1: an excited orbital of the atom

In the above wave functions, Ψ_0, $\Psi_S(i-l)$, $\Psi_T^{\frac{1}{2}}(i-l)$ and Ψ_X correspond to the ground state, the excited singlet state $\phi_s(i-l)$, the triplet state $\phi_t(i-l)$ and the excited state of the atom respectively. $\Psi_T^{\frac{3}{2}}(i-l)$ corresponds to the triplet state. $\Psi_C(i-\chi_0)$ and $\Psi_C(\chi_0-l)$ show the electron-transfer configurations from i to χ_0 and from χ_0 to l respectively.

The energies and wave functions of the resulting states of the whole system can be given by solving the secular determinant. However, in order to avoid complications, a simplification of the treatment will be undertaken.

Reactivity of Conjugated Molecules

The object in this section is to find the energy change of the ground state of the whole system arising from interaction, relative to that in a large intermolecular distance where there is no interaction between the molecule and the radical.

In some theories of the chemical reactivity of conjugated molecules which have dealt with the energy of the reacting system by explicitly taking into account the interaction between the molecule and the radical[2,6], only the effect of the electron transfer has been discussed; no discussion has been given of the effect of the exchange of electrons. It is supposed that interaction by exchange of electrons between the molecule and the radical is as important as that by electron transfer, because the bond between the molecule and the radical may have the character of a σ-bond rather than of a π-bond in the activated complex.

From this viewpoint, the problem will be treated by taking into account the following configurational wave functions of the whole system:

$$\Psi_0,\ \Psi_S(i-l),\ \Psi_T^{\frac{1}{2}}(i-l),\ \Psi_C(i-\chi_0),\ \Psi_C(\chi_0-l)$$

By applying a perturbation theory for the small interactions, the energy of the ground state, W_0, is obtained as follows:

$$\begin{aligned} W_0=&(\Psi_0\mathrm{H}\Psi_0)\\ &+\sum_i^{\mathrm{occ}}\sum_l^{\mathrm{vac}}\left\{\frac{(\Psi_0\mathrm{H}\Psi_S(i-l))^2}{(\Psi_0\mathrm{H}\Psi_0)-(\Psi_S(i-l)\mathrm{H}\Psi_S(i-l))}\right.\\ &\left.+\frac{(\Psi_0\mathrm{H}\Psi_T^{\frac{1}{2}}(i-l))^2}{(\Psi_0\mathrm{H}\Psi_0)-(\Psi_T^{\frac{1}{2}}((i-l)\mathrm{H}\Psi_T^{\frac{1}{2}}(i-l))}\right\}\\ &+\sum_i^{\mathrm{occ}}\frac{(\Psi_0\mathrm{H}\Psi_C(i-\chi_0))^2}{(\Psi_0\mathrm{H}\Psi_0)-(\Psi_C(i-\chi_0)\mathrm{H}\Psi_C(i-\chi_0))}\\ &+\sum_l^{\mathrm{vac}}\frac{(\Psi_0\mathrm{H}\Psi_C(\chi_0-l))^2}{(\Psi_0\mathrm{H}\Psi_0)(\Psi_C(\chi_0-l)\mathrm{H}\Psi_C(\chi_0-l))}\end{aligned}$$

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[4] Y. Mori, This Bulletin, **34**, 1031 (1961).
[5] Y. Mori, ibid., **34**, 1035 (1961).
[6] K. Fukui, T. Yonezawa and C. Nagata, *J. Chem. Phys.*, **27**, 1274 (1957).

Neglecting overlap integrals, the matrix elements can be written as follows:

$$(\Psi_0 \mathrm{H} \Psi_0) = E_0 - \sum_i^{\mathrm{occ}} k_{i\chi}^0$$

$$= E$$

$$(\Psi_S(i-l)\mathrm{H}\Psi_S(i-l))$$
$$= E + \Delta E_s(i-l) + 1/2(k_{i\chi}^0 - k_{l\chi}^0)$$

$$(\Psi_T^1(i-l)\mathrm{H}\Psi_T^1(i-l))$$
$$= E + \Delta E_t(i-l) + 3/2\, k_{i\chi}^0 + 1/2\, k_{l\chi}^0$$

$$(\Psi_C(i-\chi_0)\mathrm{H}\Psi_C(i-\chi_0))$$
$$= E - \varepsilon_i + a_\chi^0 + (\chi_0 \mathrm{H}_i^+ \chi_0)$$

$$(\Psi_C(\chi_0-l)\mathrm{H}\Psi_C(\chi_0-l))$$
$$= E - \varepsilon_\chi^0 + a_l + (l\mathrm{H}_\chi^+ l)$$

$$(\Psi_0\mathrm{H}\Psi_S(i-l)) = -1/\sqrt{2}\,(i\chi_0\mathrm{H}\chi_0 l)$$

$$(\Psi_0\mathrm{H}\Psi_T^1(i-l)) = \sqrt{3/2}(i\chi_0\mathrm{H}\chi_0 l)$$

$$(\Psi_0\mathrm{H}\Psi_C(i-\chi_0)) = -(i\mathrm{H}\chi_0)$$

$$(\Psi_0\mathrm{H}\Psi_C(\chi_0-l)) = (l\mathrm{H}\chi_0)$$

where E_0 is the energy of the ground state of the system without interaction, and $\Delta E_s(i-l)$ and $\Delta E_t(i-l)$ are the excitation energies of the molecule to the singlet and triplet states respectively. The integrals in these expressions are:

$$k_{i\chi}^0 = (i\chi_0\mathrm{H}\chi_0 i)$$

$$\varepsilon_i = (i\mathrm{H}_0 i)$$

$$a_l = (l\mathrm{H}_0 l) + \sum_i^{\mathrm{occ}}\{2(ll:ii) - (li:li)\}$$

$$\varepsilon_\chi^0 = (\chi_0\mathrm{H}_0\chi_0)$$

$$a_\chi^0 = (\chi_0\mathrm{H}_0\chi_0) + (\chi_0\chi_0:\chi_0\chi_0)$$

$$(\chi_0\mathrm{H}_i^+\chi_0) = (\chi_0\mathrm{H}\chi_0) - (\chi_0\mathrm{H}_0\chi_0) - (ii:\chi_0\chi_0)$$

$$(l\mathrm{H}_\chi^+ l) = (l\mathrm{H}l) - (l\mathrm{H}_0 l) - (ll:\chi_0\chi_0)$$

where H and H_0 respectively the Hamiltonian of the whole system with and without interaction between the molecule and the radical.

The integrals are reduced by disregarding non-neighbors and the difference between H and H_0 as follows:

$$(\chi_0\mathrm{H}_i^+\chi_0) = -(ii:\chi_0\chi_0)$$

$$(l\mathrm{H}_\chi^+ l) = -(ll:\chi_0\chi_0)$$

$$(i\mathrm{H}\chi_0) = C_{ir}\cdot\beta_{r\chi}^0$$

$$(l\mathrm{H}\chi_0) = C_{lr}\cdot\beta_{r\chi}^0$$

$$(i\chi_0\mathrm{H}\chi_0 l) = C_{ir}\cdot C_{lr}\cdot\alpha_{r\chi}^0$$

$$k_{i\chi}^0 = (C_{ir})^2\cdot\alpha_{r\chi}^0$$

where C_{ir} and C_{lr} are the coefficients of the r-th AO in the molecular orbitals i and l respectively; $\beta_{r\chi}^0$ is the resonance integral and $\alpha_{r\chi}^0$ is the exchange energy between the redical and the r-th atom in the molecule.

Therefore, the energy change of the ground state ΔW_0 is

$$\Delta W_0 = -1/2\cdot q_r\cdot\alpha_{r\chi}^0$$
$$-\sum_i^{\mathrm{occ}}\sum_l^{\mathrm{vac}}\left\{\frac{(C_{ir}\cdot C_{lr})^2}{\Delta E_s(i-l)+1/2(k_{i\chi}^0-k_{l\chi}^0)}\right.$$
$$\left.+\frac{(C_{ir}\cdot C_{lr})^2}{\Delta E_t(i-l)+3/2\,k_{i\chi}^0+1/2\,k_{l\chi}^0}\right\}(\alpha_{r\chi}^0)^2$$
$$-\left\{\sum_i^{\mathrm{occ}}\frac{(C_{ir})^2}{-\varepsilon_i+a_\chi^0-(ii:\chi_0\chi_0)}\right.$$
$$\left.+\sum_l^{\mathrm{vac}}\frac{(C_{lr})^2}{-\varepsilon_\chi^0+a_l-(ll:\chi_0\chi_0)}\right\}(\beta_{r\chi}^0)^2 \qquad (2)$$

wher q_r is the electron density at the position of the r-th atom in the molecule.

The first term, $-1/2\cdot q_r\cdot\alpha_{r\chi}^0$, in Eq. 2 represents the exchange repulsion between the molecule and the radical, since $\alpha_{r\chi}^0$ has a negative value. In the first bracket of Eq. 2, the first term arises from the excited singlet states, and the second term shows the effect of the triplet states of the molecule. The exchange energy gives rise to these stabilization energies. These two terms are represented by $-1/8\,\pi_{rr}^S$ and $-3/8\,\pi_{rr}^T$ respectively, which are similar to the figures for atom-atom polarizability⁷⁾. By disregarding interelectronic interaction and exchange energy, these terms can be reduced to $-1/8\,\pi_{rr}$ and $-3/8\,\pi_{rr}$, because

$$\Delta E_s(i-l) + 1/2(k_{i\chi}^0 - k_{l\chi}^0) = \varepsilon_l - \varepsilon_i$$
$$\Delta E_t(i-l) + 3/2\,k_{i\chi}^0 + 1/2\,k_{l\chi}^0 = \varepsilon_l - \varepsilon_i$$

The two terms in the second bracket of Eq. 2, arising from electron-transfer interaction, are similar to the figures for superdelocalizability⁶,⁸⁾ for a radical attack and may be abbreviated as follows:

$$\gamma_r^+ = -\sum_i^{\mathrm{occ}}\frac{(C_{ir})^2}{-\varepsilon_i+a_\chi^0-(ii:\chi_0\chi_0)}$$

$$\gamma_r^- = -\sum_l^{\mathrm{vac}}\frac{(C_{lr})^2}{-\varepsilon_\chi^0+a_l-(ll:\chi_0\chi_0)}$$

$$\gamma_r = \gamma_r^+ + \gamma_r^-$$

Using the above abbreviations, Eq. 2 can be written as follows.

$$\Delta W_0 = -1/2\cdot q_r\cdot\alpha_{r\chi}^0$$
$$+(1/8\,\pi_{rr}^S + 3/8\,\pi_{rr}^T)(\alpha_{r\chi}^0)^2 + \gamma_r(\beta_{r\chi}^0)^2 \qquad (3)$$

The uniform charge distribution for alternant

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7) C. A. Coulson and H. C. Longuet-Higgins, *Proc. Roy. Soc.*, **A191**, 39 (1947).

8) K. Fukui, K. Morokuma, T. Yonezawa and C. Nagata, *J. Chem. Phys.*, **32**, 1743 (1960).
If interelectronic repulsion is disregarded, we obtain:

$$-\gamma_r = Z_0/(\beta_{r\chi}^0)^2$$

where Z_0 is the superdelocalizability for the radical attack.

hydrocarbons has been given by Pople[9]. Therefore, in a simple approximation, the chemical reactivity of conjugated molecules for a radical attack can be determined approximately by π_{rr} and Z_0, as has been concluded by other authors[2,7,8].

Equation 2 or 3 has an interesting feature in that the chemical reactivity of molecules is affected directly by the excited states; moreover, the triplet states are more important than the excited singlet states. The importance of the triplet states is also due to the fact that a triplet state has a lower energy than that singlet state with the same electron configuration.

Quenching of Excited (^{2}P) Sodium

The experimental work by Norrish and MacF. Smith[10] on the quenching of excited sodium by hydrocarbons shows that the hydrocarbons fall into two classes according to their cross-sections for the excited sodium, as is shown in Table I. The saturated hydrocarbons have very small quenching cross-sections. On the other hand, the unsaturated hydrocarbons have large cross-sections. Hydrogen and nitrogen have the intermediate quenching cross-sections of 7.4 Å^2 and of 14.5 Å^2 respectively. These differences can be explained by the potential energy surfaces, as will be shown below.

TABLE I. QUENCHING CROSS-SECTIONS*

	Cross-section, Å^2
Hydrogen	7.4
Nitrogen	14.5
Methane	0.11
Ethane	0.17
Propane	0.2
Butane	0.3
Cyclohexane	0.4
Ethylene	44.0
Propylene	52.0
1-Butene	58.0
2-Butene	58.0
Cyclohexene	59.0
Benzene	75.0

* R. G. W. Norrish and W. MacF. Smith, *Proc. Roy. Soc.*, **A176**, 295 (1940).

The potential-energy surfaces may well be represented by taking into account the ground configuration as well as the electron-transfer configurations from the sodium atom to the molecule, because of the low ionization potential of sodium. (The excitation energy to ^{2}P of sodium is 2.12 eV., and the ionization potential is 5.14 eV.). Since the excited states of the molecules under consideration have much higher energies than the ^{2}P of sodium, the energy transfer from the sodium atom to the molecule will be disregarded. Therefore, the discussion is carried out by taking into account Ψ_0 (the ground state of the system), Ψ_X (the excited state of the sodium atom), and Ψ_C (the electron-transfer state).

Diatomic Molecules.—The quenching cross-section of hydrogen for excited sodium has been discussed theoretically by Laidler[3] and by Magee and Ri[11], who have shown the potential-energy surfaces for the sodium-hydrogen system with the aid of the VB theory. In the present work, the problem is discussed from the point of view of the transfer of the electron from the sodium atom to the molecule.

Fig. 1. The coordinate system for linear configuration in the case of diatomic molecule.

Linear Configuration. — The wave functions used are as follows[12]:

$$\begin{aligned} &^2\Sigma^+ \quad \Psi_0=\phi_0\cdot\chi_0^\alpha(3s) \\ &^2\Pi \left\{ \begin{aligned} \Psi_X^x&=\phi_0\cdot\chi_1^\alpha(3p_x) \\ \Psi_X^y&=\phi_0\cdot\chi_1^\alpha(3p_y) \end{aligned} \right. \\ &^2\Sigma^+ \quad \Psi_X^z=\phi_0\cdot\chi_1^\alpha(3p_z) \\ &\qquad\;\; \Psi_C=\phi(\chi_0-v) \end{aligned}$$

The symmetry of the electron-transfer configuration, Ψ_C, is $^2\Sigma^+$ in the case of hydrogen and $^2\Pi$ in the case of nitrogen[13].

The diagonal matrix elements are as follows:

$$(\Psi_0\mathrm{H}\Psi_0)=E_0-\sum_i^{\mathrm{occ}} k_{i\chi}^0$$

$$(\Psi_X^x\mathrm{H}\Psi_X^x)=E_0+\varDelta E(\chi_0-\chi_1)-\sum_i^{\mathrm{occ}} k_{i\chi}^x$$

$$(\Psi_X^y\mathrm{H}\Psi_X^y)=E_0+\varDelta E(\chi_0-\chi_1)-\sum_i^{\mathrm{occ}} k_{i\chi}^y$$

$$(\Psi_X^z\mathrm{H}\Psi_X^z)=E_0+\varDelta E(\chi_0-\chi_1)-\sum_i^{\mathrm{occ}} k_{i\chi}^z$$

$$(\Psi_C\mathrm{H}\Psi_C)=E_0-\varepsilon_\chi^0+a_v+(v\mathrm{H}_X^+v)$$

and the non-vanishing off-diagonal elements are, for hydrogen:

$$(\Psi_0\mathrm{H}\Psi_X^z)=-\sum_i^{\mathrm{occ}}(i\chi_0\mathrm{H}\chi_1(3p_z)\cdot i)$$

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[9] J. A. Pople, *Trans. Faraday Soc.*, **49**, 1375 (1953).

[10] R. G. Norrish and W. MacF. Smith, *Proc. Roy. Soc.*, **A176**, 295 (1940).

[11] J. L. Magee and T. Ri, *J. Chem. Phys.*, **9**, 638 (1941).

[12] The lowest vacant MO of a diatomic molecule is represented by v.

[13] The lowest vacant MO of hydrogen is $\sigma_u{}^*$, and that of nitrogen is π_g.

$$(\Psi_0 \mathrm{H} \Psi_C) = (v(\sigma_u^+) \mathrm{H} \chi_0)$$
$$(\Psi_X^z \mathrm{H} \Psi_C) = (v(\sigma_u^+) \mathrm{H} \chi_1(3p_z) \cdot i)$$

and for nitrogen:

$$(\Psi_0 \mathrm{H} \Psi_X^z) = -\sum_i^{\mathrm{occ}} (i\chi_0 \mathrm{H} \chi_1(3p_z) \cdot i)$$
$$(\Psi_X^x \mathrm{H} \Psi_C^x) = (v(\pi_g^x) \mathrm{H} \chi_1(3p_x))$$
$$(\Psi_X^y \mathrm{H} \Psi_C^y) = (v(\pi_g^y) \mathrm{H} \chi_1(3p_y))$$

The potential energy surfaces of the configurational states Ψ_0, Ψ_X^x, Ψ_X^y and Ψ_X^z are repulsive toward the approach of the sodium atom to the molecule owing to the exchange repulsion[14], and that of Ψ_C(electron-transfer state) is attractive owing to the Coulomb interaction between the negatively-charged molecule and the sodium ion. The schematic potential-energy surfaces of these configurational states may be shown by the dotted lines in Fig. 2 (for hydrogen) and in Fig. 3 (for nitrogen).

The resulting potential-energy surfaces may be shown by the full lines in the figures by the consideration of the off-diagonal matrix elements.

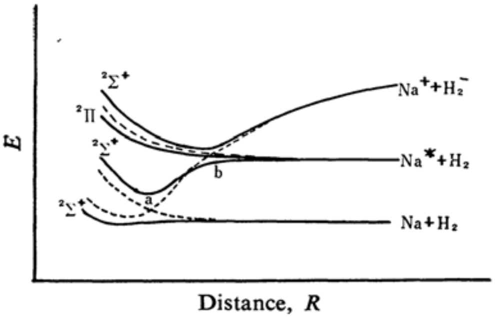

Fig. 2. The potential-energy surfaces for hydrogen (linear configuration).

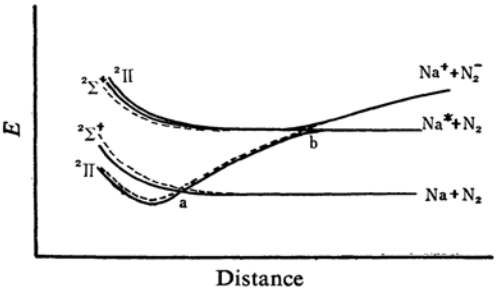

Fig. 3. The potential-energy surfaces for nitrogen (linear configuration).

The resonance splitting at a in Fig. 2 is not small, since $(v(\sigma_u^+)\mathrm{H}\chi_0)$, which is the off-diagonal element between Ψ_0 and Ψ_C, is given by the resonance integral between σ_u^+ and χ_0,

$$(v(\sigma_u^+)\mathrm{H}\chi_0) = \beta(\sigma_u^+ - \chi_0)$$

In these circumstances, the reaction system on a upper surface has a small probability of passing to a lower one via crossing[3]. The resulting lower and upper surfaces do not cross, as is shown by the full lines in Fig. 2; the quenching reaction is brought about by a radiationless transition from the upper state to the lower one, which transition gives rise to a sudden acceleration of the motion of the nuclei. This radiationless transition, however, is forbidden by the Franck-Condon principle[15] and has a small probability of occurring if the energy difference between the lower and upper states is not small.

The potential-energy surfaces for the nitrogen-sodium system shows that the quenching reaction will be brought about by a transition at crossing a. The radiationless transition at a is highly probable due to the small interaction between the lower state and the upper state (electron-transfer state); this interaction may arise from the small bending distortion of the linear configuration of the nuclei.

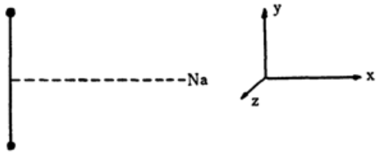

Fig. 4. The coordinate system for triangular configuration in the case of diatomic molecule.

Triangular Configuration.—In this case, the configurational wave functions and their symmetries are, for the hydrogen-sodium system, as follows:

$^2\mathrm{A}_1$	$\Psi_0 = \psi_0 \cdot \chi_0^\alpha(3s)$
$^2\mathrm{A}_1$	$\Psi_X^x = \psi_0 \cdot \chi_1^\alpha(3p_x)$
$^2\mathrm{B}_1$	$\Psi_X^y = \psi_0 \cdot \chi_1^\alpha(3p_y)$
$^2\mathrm{B}_2$	$\Psi_X^z = \psi_0 \cdot \chi_1^\alpha(3p_z)$
$^2\mathrm{B}_1$	$\Psi_C = \psi(\chi_0 - v)$

The non-vanishing interconfigurational interactions are as follows:

$$(\Psi_0 \mathrm{H} \Psi_X^x) = -\sum_i^{\mathrm{occ}} (i\chi_0 \mathrm{H} \chi_1(3p_x) \cdot i)$$
$$(\Psi_X \mathrm{H} \Psi_C) = (\sigma_u^+ \mathrm{H} \chi_1(3p_y))$$

For considerations similar to those in the

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[14] Some of the exchange energies have positive values. In the case of hydrogen, for instance, the exchange energy $k_{1\chi}$, has a positive value, since

$$k_{1\chi}^x = (1\chi_1{}^x \mathrm{H} \chi_1{}^x 1) = (1\chi_1{}^x : \chi_1{}^x 1)$$

Therefore, the surface of $\Psi_X{}^x$ for the linear configuration of the sodium-hydrogen system may be slightly attractive, but this attractive nature of the surface is unimportant in the present discussion.

[15] G. Herzberg, "Spectra of Diatomic Molecules", 2nd Ed., D. Van Nostrand Co., New York (1950).

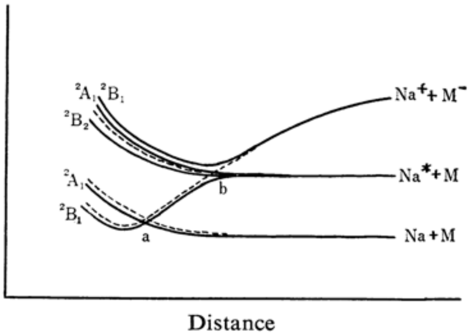

Fig. 5. The potential-energy surfaces for triangular configuration.

case of the linear configuration, the schematic potential-energy surfaces may be given as in Fig. 5. The potential-energy surface for $^2\mathrm{B}_1$ (electron-transfer state) is cut by the surface of the lowest state. Since the interconfigurational interaction will be small, the quenching reaction may be brought about by the process:

$$\mathrm{H_2 + Na^*(^2P) \rightarrow H_2 \cdots Na^*(^2B_1) \rightarrow H_2^- - Na^+ (^2B_1) \rightarrow H_2 \cdots Na(^2A_1) \rightarrow N_2 + Na(^2S)}$$

In the case of nitrogen, the wave functions, excepting those of the electron-transfer states, are similar to those of the hydrogen-sodium system. The wave functions of the electron-transfer states are as follows:

$$^2\mathbf{B}_1 \qquad \Psi_C^x = \phi(\chi_0 - v(\pi_g^x))$$

$$^2\mathbf{B}_2 \qquad \Psi_C^y = \phi(\chi_0 - v(\pi_g^y))$$

The features of these potential-energy surfaces are quite similar to those of the electron-transfer state of the hydrogen-sodium system. Both of these surfaces are cut by that of the lowest state, ($^2\mathrm{A}_1$). Therefore, the reaction system on any surface of the electron-transfer states has a large probability of passing to the lowest state via the crossing, and then the quenching reaction can proceed.

Methane. — The lowest vacant orbital of methane may belong to the irreducible representation of a_1 (totally symmetrical). In the two cases shown in Fig. 6, the wave functions of the reacting system and their symmetries are as follows:

$$^2\mathrm{A}_1 \qquad \Psi_0 = \phi_0 \cdot \chi_0^\alpha(3s)$$

$$^2\mathrm{E} \quad \begin{cases} \Psi_X^x = \phi_0 \cdot \chi_1^\alpha(3p_x) \\ \Psi_X^y = \phi_0 \cdot \chi_1^\alpha(3p_y) \end{cases}$$

$$^2\mathrm{A}_1 \quad \begin{cases} \Psi_X^z = \phi_0 \cdot \chi_1^\alpha(3p_z) \\ \Psi_C = \phi(\chi_0 - v) \end{cases}$$

Since both Ψ_0 (the lowest configuration) and Ψ_C (the electron-transfer configuration) belong to the same symmetry class, ($^2\mathrm{A}_1$), and since the interconfigurational interaction between Ψ_0 and Ψ_C is not small, it can not be expected that the resulting potential-energy surface of the upper state (the electron-transfer configuration) will be cut by that of the lowest state[16]. These circumstances are similar to those in the case of the linear configuration of the hydrogen-sodium system. The low efficiency of the quenching reaction with excited sodium will, therefore, be interpreted as due to the "non-crossing" of potential-energy surfaces.

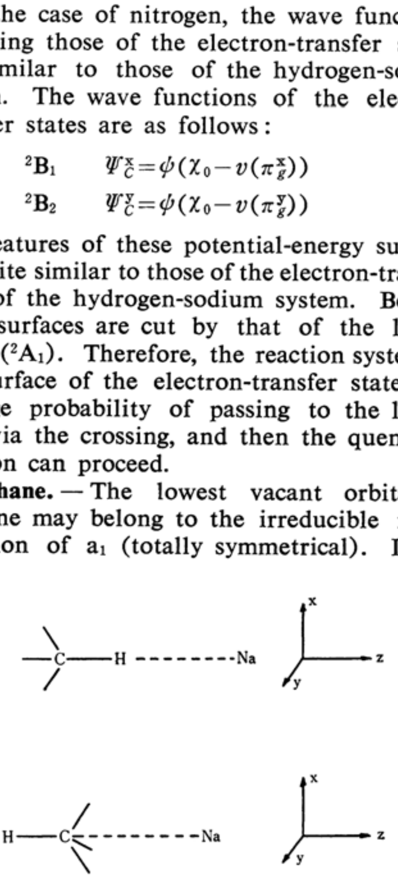

Fig. 6. The configurations for methane.

Discussion

Reactivity of Conjugated Molecules.—It has been shown that the triplet state has an effect on the chemical reactivity of conjugated molecules for a radical attack. If the energy of the lowest triplet state of a molecule is low, the role of the triplet state is clear.

The approach of a radical to a molecule causes a decrease in the exchange energy, $\alpha_{r\chi}^0$, between the radical and the r-th atom in the molecule. Since the energy difference between Ψ_0 (the lowest configuration) and $\Psi_T^1(n-n+1)$ (which corresponds to the lowest triplet state) is expressed by the relation:

$$\begin{aligned} &\Delta E_T^1(n-n+1) \\ &\quad = (\Psi_T^1(n-n+1)\mathrm{H}\Psi_T^1(n-n+1)) - (\Psi_0\mathrm{H}\Psi_0) \\ &\quad = \Delta E_t(n-n+1) + 3/2\, k_{n\chi}^0 + 1/2\, k_{n+1,\chi}^0 \\ &\quad = E_t(n-n+1) + (3/2\,|C_{nr}|^2 + 1/2\,|C_{n+1,r}|^2) \end{aligned}$$

the energy difference, $\Delta E_T^1(n-n+1)$, decreases with the approach of the radical to the molecule. When the radical approaches very close to the molecule, the energy of $\Psi_T^1(n-n+1)$ will be lower than that of Ψ_0 owing to the decrease in the exchange energy. In theses cases, the most important interconfigurational interaction is that between Ψ_0 and $\Psi_T^1(n-n+1)$, which is expressed by the nearest neighbor approximation as:

$$(\Psi_0\mathrm{H}\Psi_T^1(n-n+1)) = (C_{nr} \cdot C_{n+1,r}) \cdot \alpha_{r\chi}^0$$

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[16] Non-crossing may be due to the low electron affinity of methane.

where C_{nr} and $C_{n+1,\,r}$ are the coefficients at the r-th atom in the molecular orbitals n and $n+1$. If the activated complex or the transition state of the reaction is defined by the condition

$$\varDelta E_T^1(n-n+1)=0$$

the activation energy for the reaction may be approximated as follows:

$$\begin{aligned}\varDelta W_0 \fallingdotseq & -1/2\{\varDelta E_t(n-n+1)/(3/2\,k_{n\chi}^0 \\ & +1/2\,k_{n+1,\,\chi}^0)\}\alpha_{r\chi}^0+|C_{nr}\cdot C_{n+1,\,r}|\alpha_{r\chi}^0 \\ = & -1/2\{\varDelta E_t(n-n+1)/(3/2\,|C_{nr}|^2 \\ & +1/2|C_{n+1,\,r}|^2)\}+|C_{nr}\cdot C_{n+1,\,r}|\alpha_{r\chi}^0\end{aligned} \tag{4}$$

The experimental work by Szwarc[17] on the radical affinity of conjugated molecules has shown that the radical affinity of a conjugated molecule depends on the energy of the lowest triplet state. This result can be interpreted by Eq. 4. Equation 4 shows that the activation energy decreases with a decrease in the energy difference, $\varDelta E_t(n-n+1)$, between the ground state and the lowest triplet state.

In regard to the theoretical approximations of the present paper, the effect of the σ-bonds in the molecule was ignored completely. The use of the wave functions of the whole electron system, including the σ-electrons, would have complicated the theory and may not have affected the results greatly.

Quenching of Excited Sodium.—If the radiationless transition at a is fast, the activated state of the quenching reaction will correspond to b, which is the crossing between $\varPsi_C$ (the electron-transfer state) and $\varPsi_X$ (the excited state of sodium). The maximum value of the quenching cross section is determined by the distance between the center of the molecule and the sodium atom at b. In the case of hydrogen, the distance is found to be about 4 Å, taking the electron affinity of hydrogen as -0.28 eV.[18] This value may be compared with an experimental value of 2.7 Å$=7.4^{1/2}$ calculated from the quenching cross section (7.4 Å^2) in Table I.

The distance at b, σ, is determined mainly by the electron affinity of the molecule. Table II shows the relation between the electron affinity and the value of σ. In the calculation of the table, the small energy change of $\varPsi_X$ due to the interaction was ignored, and the integral $(v\mathrm{H}_X^{*}v)$ was approximated by $-e^2/R$, where R is the distance between the center of the molecule and the sodium atom. From this relation and by assuming that the activated state corresponds to b, the quenching cross sections of the molecules can be explained except in the case of the saturated hydrocarbons.

The lowest vacant orbital of ethylene will be the anti-bonding π orbital with the nodal plane between the two carbon atoms. The potential-energy surfaces and the quenching reaction process may be similar to those in the case of a triangular configuration for hydrogen, because the lowest state, $\varPsi_0$, and the electron-transfer state, $\varPsi_C$, have symmetry characters different from one other if the sodium atom lies in that nodal plane. Therefore, the quenching process will be as follows[19]:

$$\begin{aligned}&\mathrm{C_2H_4+Na^*(^2P)\rightarrow C_2H_4\cdots Na^*(^2B_1)}\\ &\quad\mathrm{\rightarrow C_2H_4{}^{-}\text{–}Na^*(^2B_1)\rightarrow C_2H_4\cdots Na(^2A_1)}\\ &\quad\mathrm{\rightarrow C_2H_4+Na(^2S)}\end{aligned}$$

The molecular plane of ethylene is the nodal plane of its π-orbital, but this will be unimportant since the hydrogen atoms prevent the approach of the sodium atom to the molecule.

Although the electron affinity of ethylene is unknown, the value of σ (6.6 Å) which is found from the value of the quenching cross-section in Table I can be fit into the relation shown in Table II by assuming the value of electron affinity of ethylene to be 0.9 eV.

TABLE II. THE RELATION BETWEEN σ AND ELECTRON AFFINITY

Electron affinity eV.	σ Å
-2.0	2.86
-1.0	3.57
0	4.75
1.0	7.09
2.0	13.98

The quenching cross-sections of unsaturated hydrocarbons can be explained by a consideration similar to that as in the case of ethylene. The lowest vacant orbital of the π-electrons of the unsaturated group will have the largest electron affinity in the molecule; it also has the nodal plane on which the sodium atom can approach. If the sodium atom lies in that nodal plane, the matrix element, the interconfigurational interaction between $\varPsi_0$ and $\varPsi_C$, is very small. The resonance splitting at crossing a will not be large, and hence, the radiationless transition can take place. The value of the quenching cross-section can, therefore, be determined by the electron affinity and by the size of the molecule.

The lowest vacant orbital of saturated hydrocarbons will have no nodal plane on which

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[17] M. Szwarc, *J. Chem. Phys.*, **23**, 204 (1955).

[18] I. Fisher-Hjalmars, *Arkiv Fysik*, **16**, 33 (1959).

[19] The sodium atom lies on the symmetry axis perpendicular to the molecular plane.

the sodium atom can approach. This is similar to the case of methane. The quenching cross-section of a saturated hydrocarbon may be small due to the large resonance splitting at crossing a.

It may be concluded that the efficiency of the quenching reaction with sodium (^2P) depends on the symmetry of the lowest vacant MO and on the electron affinity of the molecule.

Summary

In the first section, the chemical reactivity of conjugated molecules toward a radical attack has been explained. The index of chemical reactivity for a radical attack can be represented in terms of polarizability (π^S_{rr}, π^T_{rr}) and of γ_r, which is similar to the superdelocalizability for a radical attack. The role of the lowest triplet states of molecules in a radical reaction has been discussed.

Secondly, the quenching of excited (^2P) sodium was discussed. It has been concluded that the quenching cross-section is determined by the symmetry character of the lowest electron-transfer state and by the electron affinity of the molecule.

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