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Solvent Effects on Chemical Reactivities of Conjugated Molecules

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The propagator method is applied to the study of solvent effects on chemical reactivities of conjugated molecules. It is shoen that the number of π-electrons of a solute molecule (a conjugated molecule) controls the solvent effects on chemical reactivities. The obtained theory is applied to the study of solvent effects on selectivities of pericyclic reactions.

In recent years, a number of theoretical investigations of the solvent effects on electronic spectra and molecular structures have been made.[1-10] They can be classified in two different approaches: (1) The solvent effects are approximately described by explicitly considering one or numerous solvent molecules around the solute molecule;[1-3] (2) The virtual charge model in which the effects of solvent molecules are replaced by electrostatic continua and this allows the incorporation of the environmental effect into the Hamiltonian.[4-10]

On the other hand, there have been few theoretical studies of the solvent effects on chemical reactivities. Although reactions in the gas phase are simpler to deal with theoretically, the fact remains that most reactions occur actually in solutions. It is well known that the variation of solvent can change the rate and/or the reaction product.[11]

In this investigation it is shown that on the basis of the virtual charge model, the number of π-electrons of the solute molecule (the conjugated molecule) controls the solvent effects on the reactivities of pericyclic reactions.[12]

Hamiltonian

The reaction system in question is assumed to be well described by the following Hamiltonian[13,14] in the second quantized representation:

$$H_0 = \sum_{s} \alpha_s a_s^\dagger a_s + \sum_{s,t} \beta_{st} a_s^\dagger a_t + \sum_{q} h\omega b_q^\dagger b_q + \sum_{q} \sum_{s,t} (g_{st}^{q*} b_q^\dagger + g_{st}^q b_q) a_s^\dagger a_t, \tag{1}$$

where $a_s^\dagger$ and a_s are respectively the creation and annihilation operators for the π-electron at the s-th atom of the solute molecule, $b_g^\dagger$ and b_g are the creation and annihilation operators for the phonon with mode q, respectively, α_s is the coulomb integral, β_{st} the resonance integral, ω the phonon energy and g_{st}^q the electron-phonon interaction constant. In this model, the solvent is replaced by a phonon gas and the solvent-solute interaction by the electron-phonon interaction.[13]

The electron-photon interaction constant in Eq. 1 is defined by

$$g_{st}^q \equiv 4\pi \mathrm{i} \frac{\mathrm{e}^2 h}{2\gamma\omega} \frac{1}{\mathrm{q}} \langle s | \mathrm{e}^{\mathrm{i}\mathbf{qx}} | t \rangle, \tag{2}$$

where γ is given by the following formula;

$$\gamma \equiv \frac{4\pi}{\omega^2} \left(\frac{1}{\varepsilon_\infty} - \frac{1}{\varepsilon} \right)^{-1}, \tag{3}$$

where ε_∞ is the dielectric constant (ε) measured at the optical mode. The Hamiltonian is popular in the solid state phisics, and is successfully applied to a problem of electric resistance and so on.[14]

In this paper we neglect the mode dependence of the phonon energy. It is well known that the assumption is valid for polar media.

Propagator

In this chapter, we treat the propagator defined by

$$G_{rs}^0(t) \equiv -\mathrm{i}\langle T[a_r(t) a_s^\dagger(0)] \rangle, \tag{4}$$

where $<\cdots>$ denotes the ground state average, and T is the Wick time-ordering operator. Once the propagator is known, we can obtain the information about the eigenvalues and eigenvectors.[15,16]

We now introduce the Fourier transform of the propagator defined by

$$G_{rs}^0(z) \equiv \langle\langle a_r;\, a_s^\dagger \rangle\rangle = \int_{-\infty}^{+\infty} \mathrm{d}t\, \mathrm{e}^{\mathrm{i}zt} G_{rs}^0(t). \tag{5}$$

The Fourier transform satisfies the following equation of motion;

$$zG_{rs}^0(z) = \delta_{rs} + \langle\langle [a_r, H_0];\, a_s^\dagger \rangle\rangle, \tag{6}$$

where brackets [,] indicate a commutator. The commutation relation in Eq. 6 can be written as

$$[a_\mathrm{r}, H_0] = \alpha_r a_r + \sum_{u} \beta_{ru} a_u + \sum_{q} \sum_{u} (g_{ru}^{q*} b_q + g_{ru}^q b_u) a_u. \tag{7}$$

The substitution Eq. 17 into Eq. 6 yields

$$zG_{rs}^0(z) = \delta_{rs} + \alpha_r G_{rs}^0(z) + \sum_{u} \beta_{ru} G_{us}^0(z) + \sum_{q} \sum_{u} g_{ru}^{q*} \langle\langle b_q^\dagger a_u;\, a_s^\dagger \rangle\rangle + \sum_{q} \sum_{u} g_{ru}^q \langle\langle b_g a_u;\, a_s^\dagger \rangle\rangle. \tag{8}$$

In evaluating $G^0_{rs}(z)$ by using this equation, we have to consider the higer order propagators:

$$\begin{aligned} \mathrm{M}^{q\dagger}_{us}(z) &\equiv \ll b_q^\dagger a_u;\ a_s \gg, \\ \mathrm{M}^{q}_{us}(z) &\equiv \ll b_q a_u;\ a_s \gg. \end{aligned} \tag{9}$$

These propagators also satisfy the following equation of motion,

$$\begin{aligned} z\mathrm{M}^{q\dagger}_{us}(z) = {} & (a_u-\omega)\mathrm{M}^{q\dagger}_{us}(z) + \sum_v \beta_{uv}\mathrm{M}^{q\dagger}_{vs}(z) \\ & + \sum_l\sum_v g^{l*}_{uv} \ll b_s^\dagger b_l^\dagger a_v;\ a_s^\dagger \gg \\ & + \sum_l\sum_v g^{l}_{uv} \ll b_q^\dagger b_l a_v;\ a_s^\dagger \gg \\ & - \sum_{v,t} g^{q}_{vt} \ll a_v^\dagger a_t a_u;\ a_s^\dagger \gg. \end{aligned} \tag{10}$$

To solve the above equation we assume as follows;[16]

$$\begin{aligned} \ll b_q^\dagger b_l a_v;\ a_s^\dagger \gg &= \langle b_q^\dagger b_l \rangle \ll a_v;\ a_s^\dagger \gg \\ &= \delta_{ql} n_q \mathrm{G}^0_{vs}(z). \end{aligned} \tag{11}$$

Moreover we can assume that

$$\ll b_q^\dagger b_l^\dagger a_v;\ a_s^\dagger \gg = 0, \tag{12}$$

since the many phonon processes described by this propagator should be negligible. Further, we neglect higher order corrections to the electronic processes, that is,

$$\ll a_v^\dagger a_t a_u;\ a_s^\dagger \gg = 0. \tag{13}$$

Substituting the above approximations into Eq. 10, we obtain the following equation in the matrix notation,

$$z\mathbf{M}^{q\dagger}(z) = (\mathbf{h}-\omega)\mathbf{M}^{q\dagger}(z) + n_q\mathbf{g}^q\mathbf{G}^0(z), \tag{14}$$

or

$$\mathbf{M}^{q\dagger}(z) = n_q(z+\omega-\mathbf{h})^{-1}\mathbf{g}^q\mathbf{G}^0(z), \tag{15}$$

where

$$\mathbf{h} = \boldsymbol{\alpha} + \boldsymbol{\beta}. \tag{16}$$

Similarly $\mathbf{M}^q(z)$ is obtained as

$$\mathbf{M}^q(z) = (n_q+1)(z-\omega-\mathbf{h})^{-1}\mathbf{g}^{q*}\mathbf{G}^0(z). \tag{17}$$

Substituting Eqs. 15 and 17 into Eq. 8, we have the propagator, $\mathbf{G}^0(z)$, of the π-electron system in a solvent.

$$\begin{aligned} \mathbf{G}^0(z) = {} & [z-\mathbf{h}-\sum_q \mathbf{g}^{2*} n_q (z+\omega-\mathbf{h})^{-1}\mathbf{g}^q \\ & - \sum_q \mathbf{g}^q (n_q+1)(z-\omega-\mathbf{h})^{-1}\mathbf{g}^{q*}]^{-1}. \end{aligned} \tag{18}$$

Stabilization Energy

Let us consider a reagent, R, approaching atom r of a solvent molecule (see Fig. 1). The coulomb integral, α_s, and the resonance integral, β_{rs}, will undergo changes on approach of R. Assuming these changes or the perturbations, $\mathbf{v}$, to be small, the change of the total π-electron energy or the stabilization energy, ΔE, can be calculated by use of perturbation theory. ΔE is an energy change at the very beginning of the reaction and the reaction is expected to occur at the position where ΔE is smallest.[17]

The total π-electron energy is,

$$E_0 = \mathrm{Tr}\frac{1}{2\pi \mathrm{i}}\int_{\mathrm{c}} \mathrm{d}z\, z\mathbf{G}^0(z), \tag{19}$$

where $\mathbf{G}^0(z)$ is the matrix of the propagator, z the energy parameter and Tr the trace with respect to the arbitrary representation.[15,18] Integration contour, c, in Eq. 20 is the so-called Coulson contour shown in Fig. 2. Note that the integration includes the spin sum hereafter.

The stabilization energy[19,20] caused by the perturbation, $\mathbf{v}$, is

$$\begin{aligned} \Delta E &\equiv E - E_0 \\ &= \mathrm{Tr}\frac{1}{2\pi \mathrm{i}}\int_{\mathrm{c}} \mathrm{d}z\, z\mathbf{G}(z) - \mathrm{Tr}\frac{1}{2\pi \mathrm{i}}\int_{\mathrm{c}} \mathrm{d}z\, z\mathbf{G}^0(z) \\ &= \sum_n \frac{1}{n}\mathrm{Tr}\frac{1}{2\pi \mathrm{i}}\int_{\mathrm{c}} \mathrm{d}z \{\mathbf{G}^0(z)\mathbf{v}\}^n, \qquad (20) \\ &= -\frac{1}{2\pi \mathrm{i}}\int_{\mathrm{c}} \mathrm{d}z\, ln\, \mathrm{det}\{1-\mathbf{G}^0(z)\mathbf{v}\}, \qquad (21) \end{aligned}$$

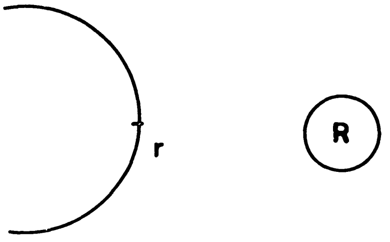

Fig. 1. R is reagent approaching a conjugated molecule.

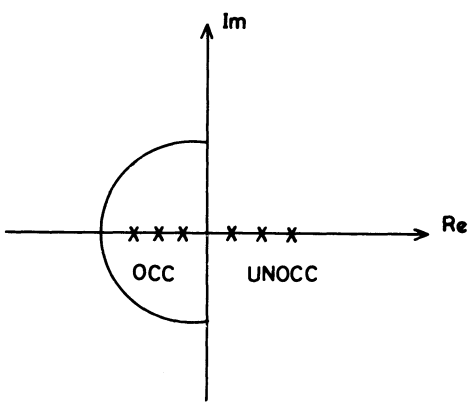

Fig. 2. Coulson contour.

where E and $\mathbf{G}(z)$ are the total π-electron energy and the propagator of the perturbed conjugated system, respectively.

It should be noted that Eqs. 20 and 21 are the straightforward generalization of the famous Coulson-Longuet-Higgins' perturbation formula.[19,21)]

The substitution Eq. 18 into Eq. 20 yields

$$\Delta E = \sum_n \frac{1}{n}\mathrm{Tr}\frac{1}{2\pi \mathrm{i}}\int_{\mathrm{c}} \mathrm{d}z[\{z-\mathbf{h}-\sum_q \mathbf{g}^{q*}n_q(z+\omega-\mathbf{h})^{-1}\mathbf{g}^q - \sum_q \mathbf{g}^q(n_q+1)(z-\omega-\mathbf{h})^{-1}\mathbf{g}^{q*}\}^{-1}\mathbf{v}]^n. \tag{22}$$

The reactivity of a chemical reaction is mainly determined by the first order term with respect to **v**.[19)] Accordingly, it is sufficient for us to study the first-order energy change

$$\Delta E^{(1)} \equiv \mathrm{Tr}\frac{1}{2\pi \mathrm{i}}\int_{\mathrm{c}} \mathrm{d}z\{z-\mathbf{h}-\sum_q \mathbf{g}^{q*}n_q(z+\omega-\mathbf{h})^{-1}\mathbf{g}^q - \sum_q \mathbf{g}^q(n_q+1)(z-\omega-\mathbf{h})^{-1}\mathbf{g}^{q*}\}^{-1}\mathbf{v}. \tag{23}$$

Equation 23 is the general formula in our theory of the solvent effects on chemical reactivities.

Pericyclic Reaction

Let us consider ring closure reactions of conjugated chains. It is well known that selection rules of ring closure reactions can be generalized to those of pericyclic reactions.[12,19)] Figure 3 shows the model of the ring closure reaction. The arrows stand for the basis functions, together with the phases.

For the sake of simplicity, let us now consider the case in which the chain is composed of n atoms and n π-electrons. If the ring closure reaction begins, the extra interaction, v, occurs between 0th and $(n-1)$th atoms:

$$v_{0,n-1} = v_{n-1,0} = v \begin{cases} >0, & \text{for the conrotatory mode} \\ <0, & \text{for the disrotatory mode.} \end{cases} \tag{24}$$

If a mode works to stabilize the solute molecule, *i.e*, $\Delta E^{(1)}<0$, we can choose this mode as the desired reaction path.

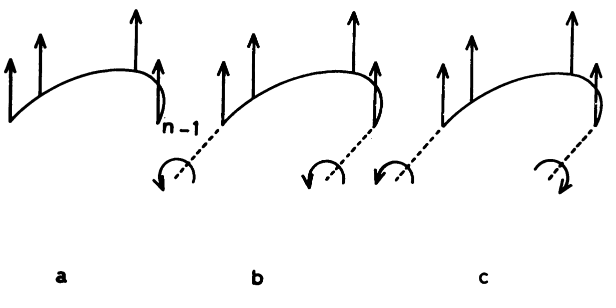

Fig. 3. Ring closure reaction, a: transition state, b: conrotatory mode, c: disrotatory mode.

The stabilization energy, $\Delta E^{(1)}$, in Eq. 23 can be expanded with respect to the electron-phonon interaction constant, $\mathbf{g}^q$,

$$\begin{aligned}\Delta E^{(1)} = {} & \mathrm{Tr}\frac{1}{2\pi \mathrm{i}}\int_{\mathrm{c}} \mathrm{d}z(z-\mathbf{h})^{-1}\mathbf{v} + \mathrm{Tr}\frac{1}{2\pi \mathrm{i}} \\ & \times \int_{\mathrm{c}} \mathrm{d}z(z-\mathbf{h})^{-1}\sum_q \mathbf{g}^{q*}n_q(z+\omega-\mathbf{h})^{-1}\mathbf{g}^q(z-\mathbf{h})^{-1}\mathbf{v} \\ & + \mathrm{Tr}\frac{1}{2\pi \mathrm{i}}\int_{\mathrm{c}} \mathrm{d}z(z-\mathbf{h})^{-1}\sum_q \mathbf{g}^q(n_q+1) \\ & \times (z-\omega-\mathbf{h})^{-1}\mathbf{g}^{q*}(z-\mathbf{h})^{-1}\mathbf{v} + \cdots. \end{aligned} \tag{25}$$

The first term of Eq. 25 determines the selection rules of electrocyclic reactions.[12)] This term has already been studied by Ohmae *et al.*[19)] The second and third terms are responsible for the solvent effects on the selection rules of electrocyclic reactions in the lowest order. Equation 25 can be rewritten as

$$\Delta E^{(1)} \cong \Delta E_{\mathrm{rule}} + \Delta E_{\mathrm{solv}}, \tag{26}$$

where

$$\Delta E_{\mathrm{rule}} \equiv \mathrm{Tr}\frac{1}{2\pi \mathrm{i}}\int_{\mathrm{c}} \mathrm{d}z(z-\mathbf{h})^{-1}\mathbf{v}, \tag{27a}$$

and

$$\begin{aligned}\Delta E_{\mathrm{solv}} \equiv {} & \mathrm{Tr}\frac{1}{2\pi \mathrm{i}}\int_{\mathrm{c}} \mathrm{d}z(z-\mathbf{h})^{-1}\sum_q \mathbf{g}^{q*}n_q(z+\omega-\mathbf{h})^{-1} \\ & \times \mathbf{g}^q(z-\mathbf{h})^{-1}\mathbf{v} + \mathrm{Tr}\frac{1}{2\pi \mathrm{i}}\int_{\mathrm{c}} \mathrm{d}z(z-\mathbf{h})^{-1} \\ & \times \sum_q \mathbf{g}^q(n_q+1)(z-\omega-\mathbf{h})^{-1}\mathbf{g}^{q*}(z-\mathbf{h})^{-1}\mathbf{v}. \end{aligned} \tag{27b}$$

First, we study the first term of Eq. 27b. We can treat this term by the representation in which the propagators are diagonal. Thus we have

$$\begin{aligned} & \mathrm{Tr}\frac{1}{2\pi \mathrm{i}}\int_{\mathrm{c}} \mathrm{d}z(z-\mathbf{h})^{-1}\sum_q \mathbf{g}^{q*}n_q(z+\omega-\mathbf{h})^{-1}(z-\mathbf{h})^{-1}\mathbf{v} \\ & = \sum_q n_q \sum_{\mathrm{i},j,k} \frac{1}{2\pi \mathrm{i}}\int_{\mathrm{c}} \mathrm{d}z\frac{1}{z-\varepsilon_{\mathrm{i}}}\mathbf{g}^{q*}_{\mathrm{i}j}\frac{1}{z+\omega-\varepsilon_j}\mathbf{g}^q_{jk}\frac{1}{z-\varepsilon_k}\mathbf{v}_{kj}, \end{aligned} \tag{28}$$

where ε_{i} is the orbital energy or the eigenvalue of **h**. Now we suppose that the electron-phonon interaction constant, g^q_{ij}, has a dominant value between the highest occupied molecular orbital, HOMO, and the lowest unoccupied molecular orbital, LUMO. Equation 28 then reduces to

$$\begin{aligned} & \sum_q n_q \sum_{\mathrm{i},j,k} \frac{1}{2\pi \mathrm{i}}\int_{\mathrm{c}} \mathrm{d}z\frac{1}{z-\varepsilon_{\mathrm{i}}}\mathbf{g}^{q*}_{\mathrm{i}j}\frac{1}{z+\omega-\varepsilon_j}\mathbf{g}^q_{jk}\frac{1}{z-\varepsilon_k}\mathbf{v}_{kj} \\ & \cong \sum_q n_q v_{\mathrm{HH}}|g^{\mathrm{q}}_{\mathrm{HL}}|^2\frac{1}{2\pi \mathrm{i}}\int_{\mathrm{c}} \mathrm{d}z\frac{1}{(z-\varepsilon_{\mathrm{H}})^2(z+\varepsilon-\varepsilon_{\mathrm{L}})} \end{aligned}$$

$$
\begin{aligned}
&+\sum_q n_q v_{\mathrm{LL}}|g^q_{\mathrm{HL}}|^2\frac{1}{2\pi \mathrm{i}}\int_{\mathrm{c}}\mathrm{d}z\frac{1}{(z-\varepsilon_{\mathrm{L}})^2(z+\omega-\varepsilon_{\mathrm{H}})}\\
&=\sum_q n_q v_{\mathrm{HH}}|g^q_{\mathrm{HL}}|^2\frac{-1}{(\varepsilon_{\mathrm{H}}-\varepsilon_{\mathrm{L}}+\omega)^2}\\
&+\sum_q n_q v_{\mathrm{LL}}|g^q_{\mathrm{HL}}|^2\frac{1}{(\varepsilon_{\mathrm{H}}-\varepsilon_{\mathrm{L}}-\omega)^2}\\
&\cong -\sum_q n_q v_{\mathrm{HH}}|g^q_{\mathrm{HL}}|^2\frac{1}{(\varepsilon_{\mathrm{H}}-\varepsilon_{\mathrm{L}}+\omega)^2},
\end{aligned}
\tag{29}
$$

where we have assumed that $(\varepsilon_{\mathrm{H}}-\varepsilon_{\mathrm{L}}-\omega)>(\varepsilon_{\mathrm{H}}-\varepsilon_{\mathrm{L}}+\omega)$, and HOMO and LUMO are given by the symbol H and L, respectively.

If we deal with the second term of Eq. 27b, the similar treatment gives

$$
\sum_q(1+n_q)v_{\mathrm{LL}}|g^q_{\mathrm{HL}}|^2\frac{1}{(\varepsilon_{\mathrm{H}}-\varepsilon_{\mathrm{L}}+\omega)^2}. \tag{30}
$$

Therefore, we have

$$
\Delta E_{\mathrm{solv}}=\sum_q|g^q_{\mathrm{HL}}|^2\frac{-n_q v_{\mathrm{HH}}+(1+n_q)v_{\mathrm{LL}}}{(\varepsilon_{\mathrm{H}}-\varepsilon_{\mathrm{L}}+\omega)^2}. \tag{31}
$$

In order to study the solvent effects on selection rules of electrocyclic reactions, it is necessary to examine v_{HH} and v_{LL}. As is shown in Eq. 24, the non-vanishing matrix elements of **v** are only $v_{0,n-1}$ and $v_{n-1,0}$ in the atomic orbital representation. We can decompose v_{AA} as follows:

$$
v_{\mathrm{AA}}=\sum_{s,t}\langle A|s\rangle\langle s|\mathbf{v}|t\rangle\langle t|A\rangle=2v_{0,n-1}p^{\mathrm{A}}_{0,n-1}, \tag{32}
$$

where $p^A_{0,n-1}$ is a partial bond order relating to the A th molecular orbital alone. The partial bond order is defined by using the propagator

$$
p^{\mathrm{A}}_{st}\equiv\frac{1}{2\pi\mathrm{i}}\int_A\mathrm{d}zg(s,t), \tag{33}
$$

$$
g(s,t)=\frac{\sin(n-t)\theta\sin(s+1)\theta}{\sin(n+1)\theta\sin\theta}, \tag{34}
$$

$$
z=2\cos\theta, \tag{35}
$$

where $g(s,t)$ is the propagator between the s th and t th atoms of the conjugated chain molecule.[22] The contour A encloses only the pole at ε_A. From these equations we get

$$
v_{\mathrm{AA}}=(-1)^A\frac{4v}{n+1}\sin^2\frac{\pi A}{n+1}, \tag{36}
$$

where

$$
A=\frac{n+1}{\pi}\cos^{-1}\frac{\varepsilon_A}{2}. \tag{37}
$$

The substitution Eq. 36 into Eq. 31 yields

$$
\begin{aligned}
\Delta E_{\mathrm{solv}}&\cong(-1)^{\mathrm{H}}v\sum_q\frac{4}{n+1}\frac{|g^q_{\mathrm{HL}}|^2}{(\varepsilon_{\mathrm{H}}-\varepsilon_{\mathrm{L}}+\omega)^2}\\
&\times\left\{n_q\sin^2\frac{\pi\mathrm{H}}{n+1}+(1+n_q)\sin^2\frac{\pi(\mathrm{H}+1)}{n+1}\right\}\\
&\propto(-1)^{\mathrm{H}}v,
\end{aligned}
\tag{38}
$$

where H is a half of the number of the π-electrons. From this equation, we can calculate the solvent effects on the selection rules of electrocyclic reactions. The results obtained are summarized in Table 1.

TABLE 1. SOLVENT EFFECTS ON THE SELECTIVITY OF THE PERICYCLIC REACTIONS

Number of electron	sign of $(-1)^{\mathrm{H}}$	sign of v[a)]	sign of ΔE_{solv}	solvent effect[b)]	selection rule
4m	+	+	+	unfavor	allowed
	+	−	−	favor	forbidden
4m+2	−	+	−	favor	forbidden
	−	−	+	unfavor	allowed

a) $v=\begin{cases}+ & \text{for conrotatory mode}\\ - & \text{for conrotatory mode}\end{cases}$

b) favor: The solvent effects accelerate the reaction
unfavor: The solvent effects disturb the reaction.

It has thus been shown that solvent effects depend on the number of π-electrons of the solute molecule only. The nature of the solvent reflects only on the magnitude of the solvent effects;

$$
|g^q_{ij}|^2\propto\left(\frac{1}{\varepsilon_\infty}-\frac{1}{\varepsilon}\right). \tag{39}
$$

It should be noted that allowed reactions are always disturbed by the solvent, but forbidden reactions are not. If we use the solvent which has the property of $|\varepsilon_\infty-\varepsilon|\gg 0$, we can expect to obtain the thermal reaction products which are the same as the photo chemical reaction ones.

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