The Spectra of Intermediates and the Mechanism of Their Formation in the Color Reactions of Polynitroanisoles with the Methoxide Ion*

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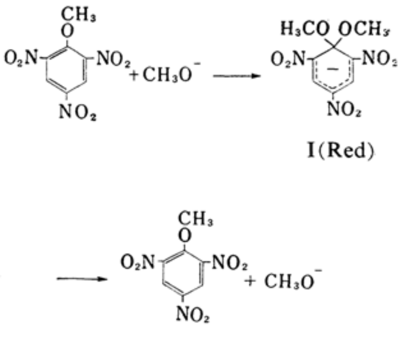
It has been reported that 2, 4, 6-trinitroanisole and 2, 4-dinitroanisole react with the methoxide (or ethoxide) ion as follows:[1-8]



(1)

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[*] Presented at the 16th Annual Meeting of the Chemical Society of Japan, Tokyo, March, 1963.

[1] T. L. Davis, "The Chemistry of Powder and Explosives," John Wiley and Sons, New York (1953), p. 171.

[2] R. C. Farmer, *J. Chem. Soc.*, **1959**, 3425, 3430.

[3] R. Foster and D. LL. Hammick, ibid., **1954**, 2153.

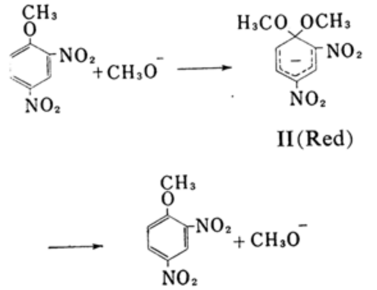
[4] R. Foster, *Nature*, **176**, 746 (1955); **183**, 1042 (1959).

[5] S. Nagakura, S. Oosawa and H. Tsubomura, presented at the Symposium on the Electronic State of Molecules, Kyoto, October, 1958.

[6] S. Nagakura and S. Oosawa, presented at the Symposium on Molecular Structure, Sapporo, August, 1960.

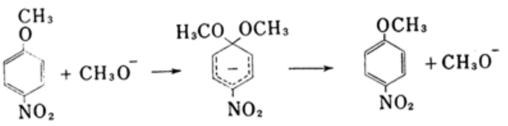
[7] L. K. Dyall, *J. Chem. Soc.*, **1960**, 5160.

[8] S. Nagakura and S. Oosawa, presented at the 13th Annual Meeting of the Chemical Society of Japan, Kyoto, April, 1960.



(2)

The colored species I is more stable than II.[8] On the other hand, it has never been found that *p*-nitroanisole gives the colored intermediate III.



(3)

The formation of Meisenheimer's intermediates I and II has been confirmed by Nagakura and Oosawa[5,8] and by Dyall[7] on the basis of the infrared spectra of these colored complexes. They indicate that the carbon atom at the seat of substitution has sp^3-hybridization. Recently the constitution of Meisenheimer's type has been widely accepted for many colored complexes of polynitrobenzene derivatives with alkalies.*

In order to interpret the formation of the above intermediates, Bunnett et al.,[9] Nagakura et al.[5,6] and Parker et al.[10,11] presented the two-stage mechanism shown in Fig. 1, for the color reactions.

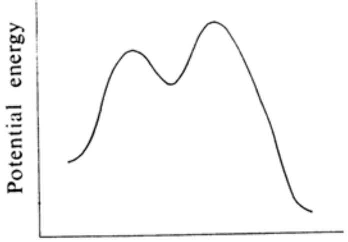


Fig. 1. The energy profile for two-stage mechanism.

From the energy level diagrams for reagents and aromatic molecules,[12] and from the above findings regarding the infrared spectra, Nagakura[13] proposed the following mechanism for the formation of an intermediate in the process of aromatic substitution:

1) A charge transfer occurs between a reagent and an aromatic compound.

2) A π-electron is localized on the carbon atom at the seat of substitution, and the atom is consequently removed from conjugation.

3) The carbon atom undergoes a change in hybridization from sp^2 to sp^3.

Recently, from the concept of Meisenheimer's intermediate complex, Miller[14] made energy calculations for the aromatic nucleophilic substitutions, utililizing bond energies, electron affinities and solvation energies.

In the present work, by means of the simple LCAO MO method, qualitative attempts will be made to account for the visible absorption spectra of Meisenheimer's intermediates I and II and for the fact that the intermediate I is more stable than II, while the intermediate III can not be observed, and to examine the possibility of the appearance of potential-energy minima on the potential energy curves for the substitutions (1)—(3).

Experimental

The Red Complex of 2, 4, 6-Trinitroanisole with Methoxide.—When a methanolic solution of sodium methoxide is added to a methanolic solution of trinitroanisole, a red solution is produced. When the resulting solution is allowed to stand at room temperature, reddish orange crystals precipitate. The spectrum of the orange methanolic solution of the crystals collected was measured as that of Meisenheimer's intermediate I. The orange solution was decolorized soon after, giving an absorption curve similar to that for 2, 4, 6-trinitroanisole.

The Red Complex of 2, 4-Dinitroanisole with Methoxide.—When dinitroanisole in methanol is treated with sodium methoxide, a red solution is formed. The spectrum of the colored solution was measured as that of Meisenheimer's intermediate II, since red-colored crystals did not precipitate from the solution. It is known that the red complex is rapidly converted, mainly into 2, 4-dinitroanisole, in methanol.[8]

The Complex of *p*-Nitroanisole with Methoxide.—When nitroanisole in methanol was treated with sodium methoxide, no colored solution was formed.

Spectra.—The spectra of the solutions were measured using a Hitachi EPU-2 spectrophotometer at room temperature.

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* For example: See Ref. 28 below; R. Foster and R. K. Mackie, *Tetrahedron*, **18**, 119, 161 (1961); **18**, 1131 (1962); *Trans. Faraday Soc.*, **58**, 860 (1962).

[9] J. F. Bunnett, E. W. Garbisch and K. M. Pruitt, *J. Am. Chem. Soc.*, **79**, 385 (1957).

[10] R. E. Parker and T. O. Read, *J. Chem. Soc.*, **1962**, 9, 2314.

[11] D. H. D. Elias and R. E. Parker, ibid., **1962**, 2616.

[12] S. Nagakura and J. Tanaka, This Bulletin, **32**, 734 (1959).

[13] S. Nagakura, *Chem. and Chem. Ind. (Japan)*, **15**, 617 (1962).

[14] J. Miller, *J. Am. Chem. Soc.*, **85**, 1628 (1963).

Results of the Measurements

The spectra measured are indicated in Fig. 2. From the above reports,[1-8] Absorption curves 1 and 2 in Fig. 2 can be considered to be due to the Meisenheimer intermediates I and II respectively. The intermediate I has two absorption maxima, at ca. 485 and 415 mμ, while the intermediate II has a maximum at ca. 495 mμ.

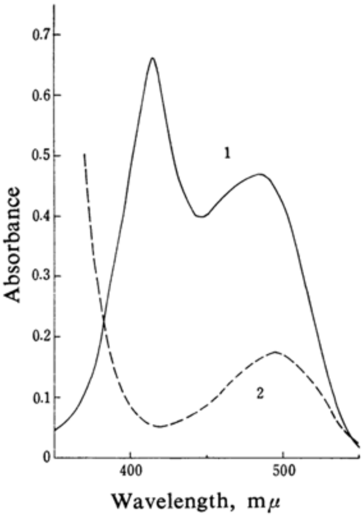

Fig. 2. Absorption spectra of Meisenheimer's intermediates in methanol (at room temperature).
1 [Trinitroanisole·CH_3O]$^-$
2 [Dinitroanisole·CH_3O]$^-$

Method of Calculation

In order to indicate the degree of proceeding of the substitution, the author has introduced the reaction parameter t, which takes continuous values from 1 through zero to -1. Let t change the values of the resonance integrals in the process of the substitution in order to represent the initial and final states at $t=1$ and -1 respectively, and in order to form Meisenheimer's intermediate at $t=0$. As Fukui et al.[15] found, the change in the electronic structure of each activated complex is assumed to be divided into two parts, a σ- and a π-part.

The resonance integrals β' and β for the σ- and π-parts respectively are assumed to be expressed as follows:

In the case of $t=1\rightarrow 0$:

σ-part, $\beta'_{C'O2}=(1-t)b'_{C'O2}\beta'_{CC}$

π-part, $\beta_{C'O1}=tb_{C'O1}\beta_{CC}$

$$\beta_{C'C}=t\beta_{CC}$$

In the case of $t=0\rightarrow -1$:

σ-part, $\beta'_{C'O1}=(1+t)b'_{C'O1}\beta'_{CC}$

π-part, $\beta_{C'O2}=-tb_{C'O2}\beta_{CC}$

$$\beta_{C'C}=-t\beta_{CC}$$

Here the suffix $_{C'}$ denotes the carbon atom at the seat of substitution, while the symbols $_{O1}$ and O2 indicate the oxygen atoms of the outgoing and ingoing CH_3O-groups respectively.

Coulomb and Resonance Parameters.—The Coulomb integrals are represented by α' and α for the σ- and π-parts respectively.

σ-Part,

for CH_3O (for which the parameters for OH[16] are used directly):

$$\alpha'_O=\alpha'_C+0.5\beta'_{CC}$$
$$b'_{C'O1}=b'_{C'O2}=0.5$$

π-Part,

for CH_3O: [17-19]

$$\alpha_O=\alpha_C+2\beta_{CC}$$
$$b_{C'O1}=b_{C'O2}=0.6$$

for NO_2: [20]

$$\alpha_N=\alpha_O=\alpha_C+\beta_{CC}$$
$$\beta_{CN}=\beta_{NO}=\beta_{CC}$$

In the present calculation the following approximations have been made for convenience:

1) The change in energy due to the change in hybridization from sp^2 to sp^3 has not been considered. This energy will be small. For instance, Coulson[21] estimated the bond energies of the CH bonds of sp^2 and sp^3 as 106 and 103 kcal./mol. respectively.

2) Hyperconjugation has been ignored.

3) The symmetry of C_{2v} has been assumed to hold for the reaction processes of p-nitroanisole and 2, 4, 6-trinitroanisole.

On the basis of the above assumptions, the energy levels of the molecular orbitals of the σ- and π-parts in the three activated complexes at $t=1\rightarrow 0\rightarrow -1$ were calculated by means of the simple LCAO MO approximation. In each complex, the molecular orbital of the σ-part was represented as a linear combination of a pseudo-π-atomic orbital of the methoxy group and one of π-atomic orbitals of the polynitroanisole, and the orbital of the π-part was

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[15] K. Fukui, T. Yonezawa and C. Nagata, This Bulletin, 27, 423 (1954); *J. Chem. Phys.*, 27, 1247 (1957).

[16] K. Fukui, H. Kato and T. Yonezawa, This Bulletin, 33, 1197 (1960).

[17] L. E. Orgel, T. L. Cottrell, W. Dick and L. E. Sutton, *Trans. Faraday Soc.*, 47, 113 (1951).

[18] S. Nagakura and T. Hosoya, This Bulletin, 25, 179 (1952).

[19] B. Pullman and A. Pullman, *Revs. Modern Phys.*, 32, 428 (1960).

[20] J. I. A. Alonso, *Compt. rend.*, 233, 403 (1951).

[21] C. A. Coulson, "Valence," Oxford University Press, Oxford (1953), p. 200.

represented as a combination of all the π-orbitals. A bonding molecular orbital of each σ-part is occupied by two electrons. The bonding molecular orbitals of the π-parts for *p*-nitroanisole, 2,4-dinitroanisole and 2,4,6-trinitroanisole are occupied by 12, 16 and 20 electrons respectively.

For example, in the case of *p*-nitroanisole at $t=1\rightarrow 0$, the x'_{ti} energy levels (in units of $(\varepsilon'_{ti}-\alpha'_{\mathrm{C}})/\beta'_{\mathrm{CC}}$) of the molecular orbitals of the σ-part and the x_{ti} levels (in units of $(\varepsilon_{ti}-\alpha_{\mathrm{C}})/\beta_{\mathrm{CC}}$) of the $\mathrm{A_1}$-molecular orbitals of the π-part are obtained from the following secular equations, 4 and 5, respectively:

For the σ-part:

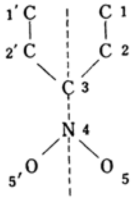
$$0=\begin{vmatrix} -x'_{ti} & 0.5(1-t) \\ 0.5(1-t) & -x'_{ti}+0.5 \end{vmatrix} \tag{4}$$

and for $\mathrm{A_1}$-orbitals of the π-part:

$$0=\begin{vmatrix} -x_{ti}+2 & 0.6t & 0 & 0 & 0 & 0 & 0 \\ 0.6t & -x_{ti} & 2t & 0 & 0 & 0 & 0 \\ 0 & t & -x_{ti} & 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & -x_{ti} & 1 & 0 & 0 \\ 0 & 0 & 0 & 2 & -x_{ti} & 1 & 0 \\ 0 & 0 & 0 & 0 & 1 & -x_{ti}+1 & 2 \\ 0 & 0 & 0 & 0 & 0 & 1 & -x_{ti}+1 \end{vmatrix}$$

$$=x_{ti}(x_{ti}-2)D_0(x_{ti})-0.6^2t^2D_0(x_{ti})+t(x_{ti}-2)D_{11}(x_{ti}) \tag{5}$$

Here $D_0(x_{ti})$ and $D_{11}(x_{ti})$ are the secular determinants of the conjugated system IV and the minor of its 11th element respectively.



IV

The energy levels for $t=0\rightarrow -1$ are symmetric to those for $t=1\rightarrow 0$ with respect to $t=0$, because the reagent and the group to be substituted are the same.

Results of Calculation

The Energy Levels of Meisenheimer's Intermediates.—The energy levels of the molecular orbitals in Meisenheimer's intermediates are obtained, as indicated in Fig. 3, by calculating the energy levels for the π-parts at $t=0$. Figure 3 shows that the excitation energies are greater in the order of 2,4-dinitroanisole, 2,4,6-trinitroanisole and *p*-nitroanisole. The excitation energy for the intermediate III is considerably greater in comparison with the others. Accordingly, even if the intermediate III should be formed, its longer absorption would not appear in the visible region. It can be expected that the two absorption bands of the intermediate I will appear at the longer wave lengths, because the second lowest vacant orbital lies close to the lowest one. The above predictions qualitatively agree with the experimental results.

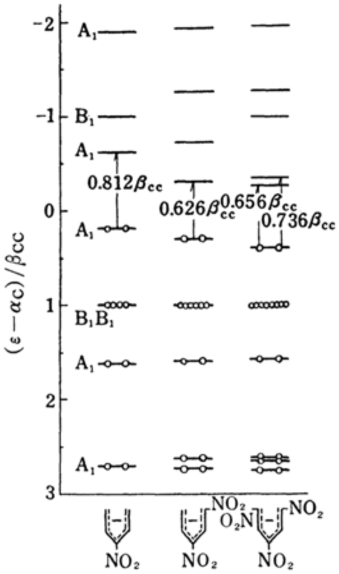


Fig. 3. The energy levels and transitions of π-electrons in Meisenheimer's intermediates.

The Change in the Occupied Orbital Energy of the σ-Part.—The occupied orbital energy ε'_t of the σ-part is obtained from the secular Eq. 4. If the value of ε'_t at $t=1$ is represented as ε'_1, the change in the energy of the σ-part at t can be obtained from:

$$(\varepsilon'_t-\varepsilon'_1)=(x'_t-x'_1)\beta'_{\mathrm{CC}} \tag{6}$$

Figure 4 is drawn by calculating according to

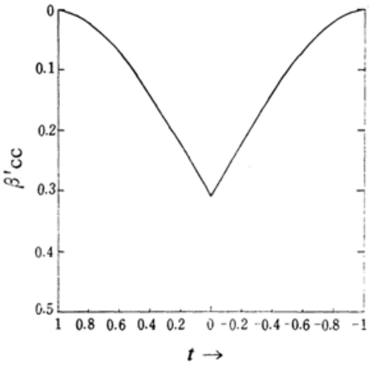


Fig. 4. The change in the occupied orbital energy of each σ-part.

Eq. 6. Of course, the energy of the σ-part is the lowest at $t=0$, because the reagent CH_3O^- is covelently bound to the nucleus of each polynitroanisole.

The Changes in the Occupied Orbital Energies of the π-Parts.—The ε_{ti} energies of the occupied molecular orbitals in the activated complex of each polynitroanisole are indicated in Figs. 5—7. As may easily be seen in these figures, the change in the orbital energy with t is the greatest in the highest occupied orbital. The second greatest change is found for the orbital with the energy value of 2 at $t=0$. These orbitals are to be ascribed to the methoxy groups to be substituted.

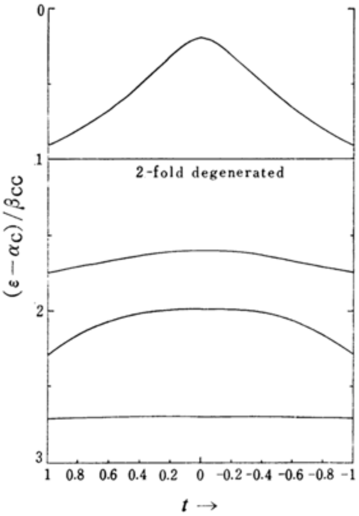


Fig. 5. The change in the occupied orbital energy levels of the π-part for nitroanisole.

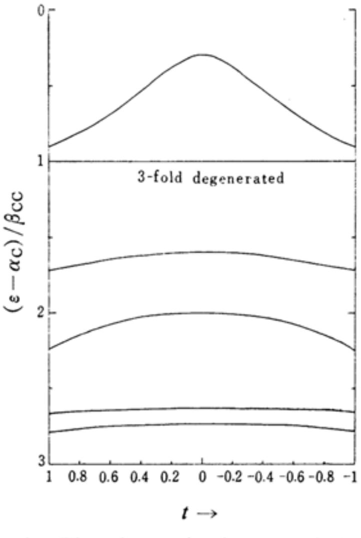


Fig. 6. The change in the occupied orbital energy levels of the π-part for dinitroanisole.

If ε_{1i} denotes the value of ε_{ti} at $t=1$, the change in the electronic energy of the π-part of each polynitroanisole can be given as:

$$\sum_i^{occu}(\varepsilon_{ti}-\varepsilon_{1i})=\sum_i^{occu}(x_{ti}-x_{1i})\beta_{CC} \tag{7}$$

The results calculated are shown in Fig. 8. It is reasonable that the change in the electronic energy of each π-part is at its maximum at $t=0$, because the conjugated system is at its minimum at $t=0$. It follows from Fig. 8 that the changes in the energies of the π-parts are

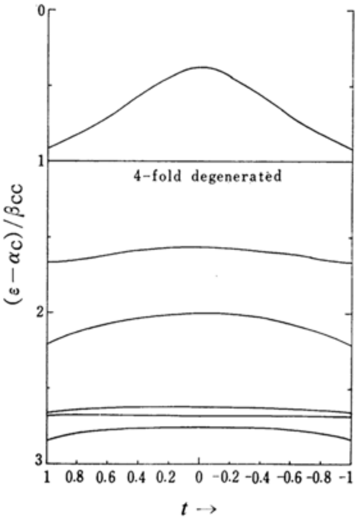


Fig. 7. The change in the occupied orbital energy levels of the π-part for trinitroanisole.

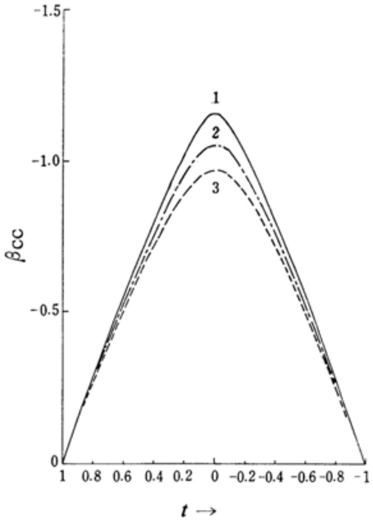


Fig. 8. The changes in electronic energies of the π-parts.
1 Nitroanisole
2 Dinitroanisole
3 Trinitroanisole

smaller with the increasing numbers of nitro groups.

The Total Changes in Electronic Energies.— By adding Eq. 6 to Eq. 7, the total change in the electronic energy of the activated complex of each polynitroanisole at t is given as

$$(\varepsilon'_t-\varepsilon'_1)+\sum_i^{occu}(\varepsilon_{ti}-\varepsilon_{1i})=(x'_t-x'_1)\beta'_{\mathrm{CC}}+\sum_i^{occu}(x_{ti}-x_{1i})\beta_{\mathrm{CC}} \qquad (8)$$

By using $\beta'_{\mathrm{CC}}=-6.364$ eV.[22] and $\beta_{\mathrm{CC}}=-3$ eV.,* one can find the total changes in electronic energies according to Eq. 8, as is indicated in Fig. 9. It can be seen from Fig. 9 that the activation energies for the formation of the intermediates become smaller as the numbers of nitro groups increase, and that the stabilization energies at $t=0$ are similarly greater. These lead to the expectation that, in the color reactions of the polynitroanisoles with the methoxide ion, the colored intermediates are more easily formed and more stable as the numbers of nitro groups increase. In fact, it has been observed that the intermediates are stable in the order of the increasing numbers of nitro groups. It may also be expected from Fig. 9 that Meisenheimer's intermediate III of p-nitroanisole with the methoxide ion is the hardest to form because the energy of activation is the greatest and the stabilization energy at $t=0$ is the smallest in the case of p-nitroanisole.

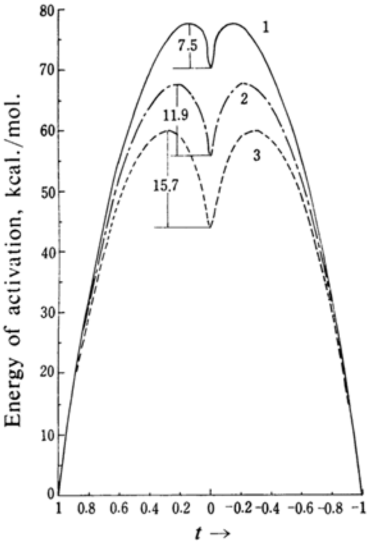


Fig. 9. The total changes in electronic energies.
1 Nitroanisole 2 Dinitroanisole
3 Trinitroanisole

Discussion

As has been mentioned above, the results of the calculation show that the energies of activation for the formation of Meisenheimer's intermediates becomes smaller with the increasing numbers of nitro groups. This is in accordance with the experimental results[23-26] for the similar reactions of polynitrobenzene derivatives.

The fact that the intermediate II is more labile than I can be ascribed to the low stabilization energy of II. Because of the low energy, the intermediate II is more easily converted into 2, 4-dinitroanisole than is I, although the energy of activation for the formation of II is higher than that for I.

Nagakura, Oosawa and Tsubomura[5] reported that the energy of activation for the decomposition of Meisenheimer's complex of 2, 4-dinitroanisole with hydroxyl ions to 2, 4-dinitroanisole is 15.0 kcal./mol. The corresponding energy for 2, 4-dinitroanisole is calculated as 11.9 kcal./mol. in the present work.

The changes in π-electronic energies in the polynitroanisoles at $t=0$, calculated according to Eq. 7, are equal to the localization energies presented by Wheland.[27] Accordingly, the energies of activation for the formation of the three activated complexes are governed by the localization energies, since the changes in energy for the three 6-parts are the same in the calculation. These energies of activation are mainly dependent on the greatest changes of the highest-occupied orbital energies for the π-parts, as is indicated in Figs. 5—7.

The present calculation is too rough to predict the observed values. The following points must be considered in order to calculate them more precisely:

1) It is better to represent the molecular orbital of each activated complex as a combination of all the 2pπ-orbitals of each polynitroanisole and the atomic orbital of the reagent.

2) The change in hybridization, $sp^2 \rightarrow sp^3 \rightarrow sp^2$, in the carbon atom at the seat of substitution must be considered.[13]

3) A calculation including hyperconjugation might possibly afford a somewhat smaller

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[22] K. Fukui, H. Kato and T. Yonezawa, This Bulletin, 33, 1197 (1960).

* This value has often been used in the simple LCAO MO approach.

[23] J. Miller, *J. Chem. Soc.*, **1952**, 3550.

[24] R. E. Parker and T. O. Read, ibid., **1962**, **9**, 3149.

[25] D. H. D. Elias and R. E. Parker, ibid., **1962**, 2616.

[26] L. F. Fieser and M. Fieser, "Textbook of Organic Chemistry," Maruzen, Tokyo (1952), p. 458.

[27] G. W. Wheland, *J. Am. Chem. Soc.*, **64**, 900 (1942).

change in the energy of each π-part.

4) It is necessary to examine the parameters of the coulomb and resonance integrals used.

According to the energy level diagrams of Nagakura and Tanaka,[12] the highest-occupied orbital energy in the methoxy ion CH_3O^- is higher than the lowest vacant one for each polynitroanisole. The parameter of the coulomb integral for the methoxy group used in the present calculation is one for the methoxy radical $CH_3O\cdot$. Miller[14] estimated the loss of the electron affinity of $-O^-$ as -61 kcal. It is necessary to change the coulomb parameter for the methoxy group from CH_3O^- to $CH_3O\cdot$ with t.

5) If configuration interaction is included, the difference between the two excitation energies for the intermediate I will be calculated as somewhat greater.

6) The solvent effect can not be neglected, because the effect on the spectra and life-times of Meisenheimer's intermediates are considerable.[28] According to Miller's calculation, the solvation energy for these intermediates was estimated as 54 kcal. He calculated the activation energies as 14, 19.5 and 25.5 kcal. for reactions 1—3 respectively. In comparison with these values, the corresponding values in the present calculation are much greater. This is possibly due to the neglect of the solvent effect in the calculation.

7) Steric hindrance must be considered.

Summary

By the simple LCAO MO treatment, introducing the reaction parameter, the following expectations have been obtained for the color reactions of polynitroanisoles with the methoxide ion: 1) Meisenheimer's intermediates are more easily formed and are more stable as the numbers of nitro groups increase. 2) The energies of activation for the formation of the intermediates become smaller as the numbers of nitro groups increase. These expectations are in agreement with the experimental results.

The author is particularly indebted to Professor Hiroshi Azumi, Professor Yoshito Amako and Dr. Shigeyoshi Katagiri for his discussions with them.

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[28] T. Abe, This Bulletin, **34**, 21, 1776 (1961).