Electronic Spectra of Polynitrophenols and their Anions

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(Received June 26, 1961)

In previous papers[1] it has been reported that, for *m*-dinitro- and 1, 3, 5-trinitro-benzene, a 260 mμ band of nitrobenzene shifted toward blue in the order of the increasing numbers of the nitro group, although substitution had been considered to shift in general the absorption of a parent molecule to longer wavelengths. High-intensity absorption bands of mono- and di-substituted benzenes, each containing only a strongly electron-attracting substituent, have been interpreted by Nagakura and Tanaka[2-5] in terms of the intramolecular charge transfer spectra. In the present paper, an attempt has been made to expand Nagakura and Tanaka's theory into high-intensity absorption bands of polynitrophenols and their anions, which contain two or three electron-attracting substituents. The absorption spectra of the polynitrophenols and their anions have been indicated in the Landolt-Börnstein table[6]. However, the spectra are not complete. In this work, the absorption spectra of *p*-nitrophenol, 2, 4-dinitrophenol and picric acid, all in water, were measured, if necessary, in the presence of either hydrochloric acid or sodium hydroxide in order to obtain the spectra of these polynitrophenols and their anions.

Experimental

Commercial grade polynitrophenols were recrystallized several times from water. Commercial grade hydrochloric acid and sodium hydroxide were used without further purification. The spectra of solutions were measured using a Hitachi EPU-2 spectrophotometer at room temperature. The length of absorption cells was 1 cm.

Results

The results of the measurements of the absorption spectra are shown in Fig. 1 and Table I. The spectrum of an aqueous picric acid solution (2.69×10^{-5} M) containing hydrochloric acid at a concentration 4.8 N is considered to be due almost entirely to the undissociated picric acid, because the spectrum is nearly identical with that of a hydrochloric acid concentration of 7.2 N. Therefore, *p*-nitrophenol and 2, 4-dinitrophenol, whose dissociation constants are smaller than that of picric acid, are not dissociated in water containing 4.8 N hydrochloric acid. Aqueous solutions both of 4.8 N hydrochloric acid and of 4.2×10^{-2} N sodium hydroxide scarcely absorb in wavelength regions above 230 mμ. An absorption at 31300 cm^{-1} for *p*-nitrophenol is only slightly more intense in the aqueous hydrochloric acid solution (4.8 N) than in pure water, so that it is known that *p*-nitrophenol is mostly undissociated in water at room temperature (ca. 25°C). 2, 4-Dinitrophenol absorbs somewhat more strongly at 27600 cm^{-1} and slightly more weakly at

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[1] T. Abe, This Bulletin, **31**, 904 (1958); **32**, 339 (1959); **33**, 220 (1960).

[2] S. Nagakura and J. Tanaka, *J. Chem. Phys.*, **22**, 236 (1954); *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **75**, 331 (1954).

[3] S. Nagakura, ibid., **75**, 822 (1954); *J. Chem. Phys.*, **23**, 1441 (1955).

[4] J. Tanaka and S. Nagakura, ibid., **24**, 1274 (1956); *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **78**, 1200 (1957).

[5] J. Tanaka, S. Nagakura and M. Kobayashi, *J. Chem. Phys.*, **24**, 311 (1956).

[6] Landolt-Börnstein, " Physikalisch-chemische Tabellen ", 6th Ed., Part 3 (II), Springer, Berlin (1951), p. 269.

TABLE I. ULTRAVIOLET ABSORPTION BANDS OF THE POLYNITROPHENOLS AND THEIR ANIONS (IN cm^{-1})

p-Nitrophenol	31300*	44300			
p-Nitrophenolate anion	24900*	38000^{s}	41000^{s}		
2, 4-Dinitrophenol	33000^{s}	37900*			
2, 4-Dinitrophenolate anion	25000^{s}	27600*	38600 ?	45000	
Picric acid	29100	35000^{s}	42000*		
Picrate anion		25000^{s}	28300*	41000^{s}	45000^{s}

The marks of * and ^{s} denote the long wavelength absorption maxima (except for the case of picric acid) and the absorption shoulders, respectively.

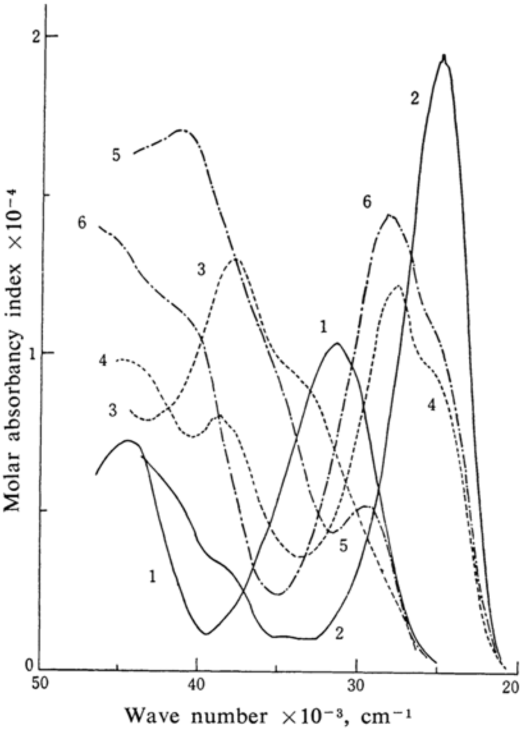

Fig. 1. Absorption spectra of aqueous solutions of the polynitrophenols.

1 An aqueous solution of *p*-nitrophenol (*p*-nitrophenol)
2 An aqueous 4.2×10^{-2} N sodium hydroxide solution of *p*-nitrophenol (*p*-nitrophenolate anion)
3 An aqueous 4.8 N hydrochloric acid solution of 2, 4-dinitrophenol (2, 4-dinitrophenol)
4 An aqueous solution of 2, 4-dinitrophenol (2, 4-dinitrophenolate anion)
5 An aqueous 4.8 N hydrochloric acid solution of picric acid (picric acid)
6 An aqueous solution of picric acid (picrate anion)

38600 cm^{-1} in the aqueous sodium hydroxide solution (4.2×10^{-2} N) than in water. From this it follows that 2, 4-dinitrophenol (2.77×10^{-5} M) is dissociated to a large extent in water at room temperature, giving the 27600 cm^{-1} band, although it is not so distinct that the 2, 4-dinitrophenolate anion also gives a band at 38600 cm^{-1}. A 28300 cm^{-1} band of picric acid has almost the same intensity in water as in an aqueous sodium hydroxide solution (4.2×10^{-2} N). This means that picric acid (2.69×10^{-5} M) is almost dissociated in water at room temperature. From the above results one can conclude that the absorption curves 1—6 in Fig. 1 are due to *p*-nitrophenol, *p*-nitrophenolate anion, 2, 4-dinitrophenol, 2, 4-dinitrophenolate anion, picric acid and picrate anion respectively, except for the 38600 cm^{-1} band in absorption curve 4.

In the present work, the absorption spectra of both 2, 4-dinitrophenol and picric acid may probably be affected both by intramolecular hydrogen bonds and by intermolecular ones, since it is well known that the formation of a hydrogen bond has an effect on the near ultraviolet absorption spectra of many aromatic compounds*.

In addition to the hydrogen bonds, it is to be expected that, in both 2, 4-dinitrophenol and picric acid, steric hindrances between the hydroxyl groups and the adjacent nitro groups will occur, affecting their spectra.

According to the Landolt-Börnstein table⁶⁾, *p*-nitrophenol and its anion show absorption shoulders near 36000 and 28000 cm^{-1} respectivery. These shoulders, although they seem to appear, can not be perceived distinctly in absorption curves 1 and 2 in Fig. 1.

From Fig. 1 and Table I one can see that the long wavelength absorption maxima of the polynitrophenols shift toward blue in the order of *p*-nitrophenol, 2, 4-dinitrophenol and picric acid, all having increasing molar absorbancy indexes in the same order, and that the absorption maxima of these polynitrophenolate anions similarly shift toward blue with the increasing number of the nitro groups. The absorption maximum of each anion lies at a longer wavelength than does that of the corresponding polynitrophenol. This red shift is greater with the increasing number of the nitro group.

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* For example: a) S. Nagakura and H. Baba, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **71**, 527, 560, 610 (1950); **72**, 3 (1951); *J. Am. Chem. Soc.*, **74**, 5693 (1952). b) N. D. Coggeshall and E. M. Lang, ibid., **70**, 3233 (1948).

Discussion

The longer wavelength absorption maximum of *p*-nitrophenol has been interpreted by Nagakura and Tanaka[3,4] in terms of the intramolecular charge transfer involving an excitation of a bonding π-electron of the highest occupied energy-level of phenol to a vacant energy-level of the nitro group, as illustrated in Fig. 2. According to Nagakura and Tanaka's theory[2-5], all high intensity absorption bands of the polynitrophenols and their anions may be similarly interpreted as due to intramolecular charge transfers. From the viewpoint of the theory, these bands will be briefly discussed below.

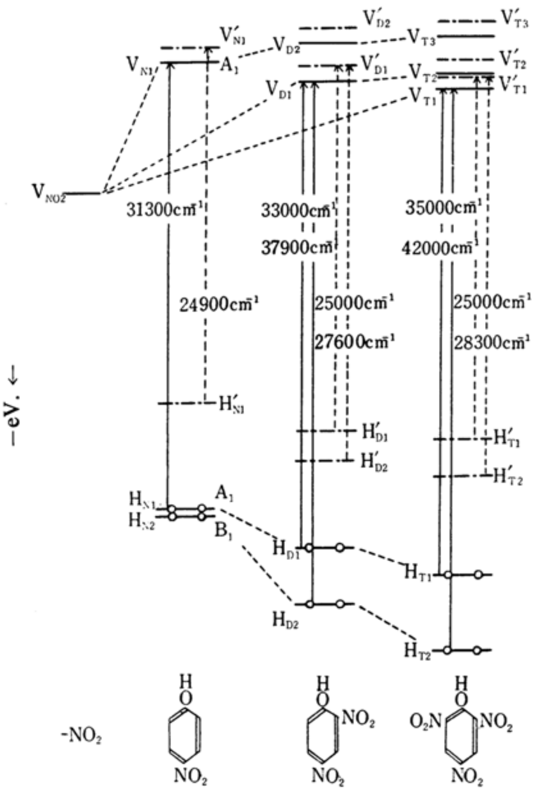

Fig. 2. The highest occupied and lowest vacant energy-levels for the polynitrophenols (——) and their anions (—·—).

When one more nitro group is substituted for hydrogen in a 2-carbon atom of *p*-nitrophenol, the highest occupied π-levels (H_{N1} and H_{N2}) of *p*-nitrophenol can be expected to interact mainly with the vacant energy-level V_{NO2} of the second entering nitro group, because both H_{N1} and H_{N2} are widely separated from the occupied energy-levels of the nitro group or have no interaction with them. H_{N1} lies close to H_{N2}. According to Nagakura and Tanaka, as the result of the interaction with V_{NO2}, the highest occupied energy-level H_N ($=H_{N1}$ or H_{N2}) is shifted by the following amount:

$$\varDelta E_N = 1/2\cdot[(V_{NO2}-H_N) - \{(H_N-V_{NO2})^2+4C_N{}^2C_{NO2}{}^2\beta^2\}^{1/2}] \quad (1)$$

Here C_N is a coefficient of an atomic orbital of the 2-carbon atom in a molecular orbital of H_N, C_{NO2}, a coefficient of an atomic orbital of a nitrogen atom in a molecular orbital of V_{NO2}, and β, a resonance integral between the two atomic orbitals of the carbon atom and the nitrogen. Similarly, V_{NO2} may interact mainly with H_{N1}, H_{N2} and V_{N1}, which are relatively near V_{NO2}. V_{N1} is the lowest vacant energy-level in *p*-nitrophenol. In 2, 4-dinitrophenol, therefore, V_{NO2} of the second nitro group may be sifted as follows:

$$\begin{aligned}\varDelta E_{NO2} = 1/2\cdot&[(H_{N1}-V_{NO2})\\&+\{(H_{N1}-V_{NO2})^2+4C_{N1}{}^2C_{NO2}{}^2\beta^2\}^{1/2}]\\&+1/2\cdot[(H_{N2}-V_{NO2})\\&+\{(H_{N2}-V_{NO2})^2+4C_{N2}{}^2C_{NO2}{}^2\beta^2\}^{1/2}]\\&+1/2\cdot[(V_{N1}-V_{NO2})\\&-\{(V_{N1}-V_{NO2})^2+4C_{VN1}{}^2C_{NO2}{}^2\beta^2\}^{1/2}]\end{aligned} \quad (2)$$

in which formula C_{VN1} is a coefficient of an atomic orbital of the 2-carbon atom in a molecular orbital of V_{N1}. By the simple LCAO MO method Nagakura[3] calculated the square values of the coefficients for *p*-nitrophenol as $C_{N1}{}^2=0.100$, $C_{N2}{}^2=0.250$ and $C_{VN1}{}^2=0.009$. By putting these values in Eq. (1), one knows that H_{N2} interacts more strongly with V_{NO2} than does H_{N1}. This suggests that an intramolecular charge transfer band due to an $H_{N2}\rightarrow V_{NO2}$ ($H_{D2}\rightarrow V_{D1}$) transition appears at a shorter wavelength than that for an $H_{N1}\rightarrow V_{NO2}$ ($H_{D1}\rightarrow V_{D1}$) transition. The two bands at 33000 and 379000 cm^{-1} for 2, 4-dinitrophenol may be associated with the transitions, $H_{D1}\rightarrow V_{D1}$ and $H_{D2}\rightarrow V_{D1}$, respectively. According to Eq. 2, the main interactions of V_{NO2} with H_{N1} and H_{N2} can be expected to raise V_{NO2} considerably, since $C_{VN1}{}^2$ is negligibly smaller than either $C_{N1}{}^2$ or $C_{N2}{}^2$. The support for this expectation comes from the fact that the band due to the $H_{D1}\rightarrow V_{D1}$ transition in dinitrophenol is at a shorter wavelength than for the $H_{N1}\rightarrow V_{N1}$ transition in nitrophenol; from this blue shift it follows that $(H_{N1}-H_{D1})>(V_{N1}-V_{D2})$. From the above discussion, the observed 33000 and 37900 cm^{-1} bands of 2, 4-dinitrophenol may be interpreted as indicated in Fig. 2.

Next, the substitution of the third nitro group in a 6-carbon atom of 2, 4-dinitrophenol can be roughly thought to move H_{D1}, H_{D2} and

V_{D1} of dinitrophenol and V_{NO2} of the third nitro group in the same directions by the same mechanism as for the substitution of the second nitro group in *p*-nitrophenol, since picric acid belongs to the symmetry group C_{2V}. It is, however, to be expected that the square values of the coefficients of the 6-carbon atom in the molecular orbitals of H_{D1} and H_{D2} in 2, 4-dinitrophenol are smaller than C^2_{N1} and C^2_{N2} respectively, owing to the strong electron-attracting nature of the second entering nitro group. Moreover, interactions of V_{NO2} of the third nitro group with V_{D1} and V_{D2}, although weak, may lower the V_{NO2}. Accordingly, it may be expected that H_{D1} and H_{D2} of dinitrophenol and V_{NO2} of the third nitro group are shifted to a lesser extent in picric acid than H_{N1} and H_{N2} of *p*-nitrophenol and V_{NO2} of the second nitro group in 2, 4-dinitrophenol respectively. Consequently, one may predict that the intramolecular charge transfer bands due to the $H_{T1} \rightarrow V_{T1}$ and $H_{T2} \rightarrow V_{T1}$ transitions in picric acid will appear at shorter wavelengths than do those for the $H_{D1} \rightarrow V_{D1}$ and $H_{D2} \rightarrow V_{D1}$ transitions respectively, although the respective blue shifts are smaller than the corresponding shifts of *p*-nitrophenol for 2, 4-dinitrophenol. The $H_{T1} \rightarrow V_{T1}$ and $H_{T2} \rightarrow V_{T1}$ transitions are most likely to produce high-intensity bands at 35000 and 42000 cm^{-1} respectively. The above expectation is in agreement with the experimental result.

In addition to the above intramolecular charge transfer bands, absorption bands due to the transitions $H_{D1} \rightarrow V_{D2}$ and $H_{D2} \rightarrow V_{D2}$ in 2, 4-dinitrophenol and those due to the transitions $H_{T1} \rightarrow V_{T2}$, $H_{T2} \rightarrow V_{T2}$, $H_{T1} \rightarrow V_{T3}$ and $H_{T2} \rightarrow V_{T3}$ in picric acid would be expected to appear, although they are not distinguished in Fig. 1.

A predominating difference in π-electron structure between each polynitrophenol and its anion can be ascribed to the fact that the electronegativity of an oxygen atom belonging to the hydroxyl group in the polynitrophenol is greater than that for the polynitrophenolate anion. It may, therefore, be approximately assumed that the dissociation of each polynitrophenol reduces only the coulomb term for the oxygen atom by $\Delta\alpha_0$ through the decrease in electronegatively. Then, according to Coulson and Longuet-Higgins[7], if an inductive effect is disregarded, each orbital of the polynitrophenol is raised by the following amount in the polynitrophenolate anion:

$$\Delta E = C_0{}^2 \cdot \Delta\alpha_0 \tag{3}$$

Here C_0 is a coefficient of an atomic orbital of the oxygen atom belonging to the hydroxyl group in the molecular orbital of each level.

The calculation[3] for *p*-nitrophenol gave values of $C_0{}^2$ for H_{N1}, H_{N2} and V_{N1} of 0.127, 0 and 0.012 respectively. Putting these values in Eq. 3, it follows that in *p*-nitrophenolate anion H_{N1} is raised more greatly than V_{N1}. It is, therefore, to be expected that an intramolecular charge transfer band of *p*-nitrophenolate anion appears at a longer wavelength than that of *p*-nitrophenol. This agrees with the experimental data.

The great red shifts of the high-intensity absorptions of 2, 4-dinitrophenol on dissociation lead to the suggestion that, in 2, 4-dinitrophenolate anion, H_{D1} and H_{D2} are raised more greatly to H'_{D1} and H'_{D2} respectively than V_{D1} and V_{D2}, as is shown in Fig. 2. The 25000 and 27600 cm^{-1} bands are possibly asssigned to the transitions $H'_{D1} \rightarrow V'_{D1}$ and $H'_{D2} \rightarrow V'_{D1}$ respectively.

When picric acid is dissociated, the energy-levels of picric acid may be raised in the same way as in the case of 2, 4-dinitrophenol. The transitions indicated by the dotted lines in Fig. 2 may produce the observed 25000 and 28300 cm^{-1} bands.

The red shifts of the intramolecular charge transfer bands of each polynitrophenol for its anion are greater with the increasing number of the nitro group. This means that the two highest occupied orbitals of each polynitrophenol are more greatly raised in its anion as the number of the nitro group increases. This, with Eq. 3, suggests that the values of $C_0{}^2$ in the molecular orbitals of these occupied levels in each polynitrophenol are greater with the increasing number of the nitro group.

Summary

The absorption spectra of *p*-nitrophenol, 2, 4-dinitrophenol, picric acid and their anions, all in water, were measured in the presence or absence of either hydrochloric acid or sodium hydroxide. The long wavelength absorption maxima of these polynitrophenols shift toward blue in the order of *p*-nitrophenol, 2, 4-dinitrophenol and picric acid, with increasing molar absorbancy indexes in the same order. The absorption maxima of the anions similarly shift toward blue. The absorption maxima of each anion lie at longer wavelengths than do those of the corresponding polynitrophenol. These red shifts are greater with the increasing number of the nitro group. The high-intensity bands of these nitro compounds containing two or three electron-attracting substituents are interpreted from the viewpoint of Nagakura and Tanaka's theory of the intramolecular charge transfer spectra.

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

The author is particularly indebted to Professor Yōkan Nomura for his suggestions and encouragement.

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