# The Absorption Spectra of 2, 4, 6-Trinitroanisole in Methanolic Sodium Methoxide

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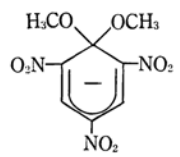
It has been reported that the absorption spectrum of a colored methanolic solution of 2, 4, 6-trinitroanisole in the presence of sodium methoxide is due to the Meisenheimer complex I.[1-4] In the present work, an attempt has been made to investigate the further interaction of 2, 4, 6-trinitroanisole with the methoxide ion at very high methoxide concentrations. For this purpose, the author measured the spectra of the colored solutions at various methoxide concentrations, using a Hitachi EPU-2A spectrophotometer at room temperature. The solutions were left to stand for half an hour before




I

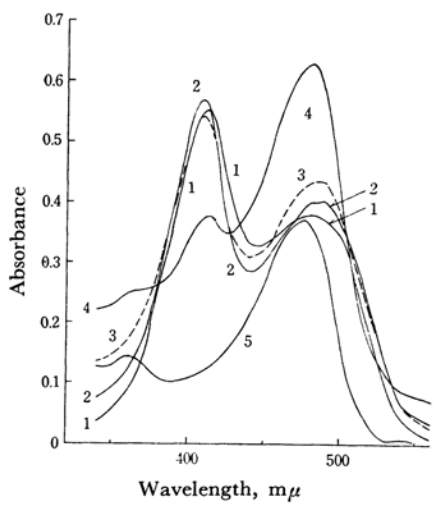


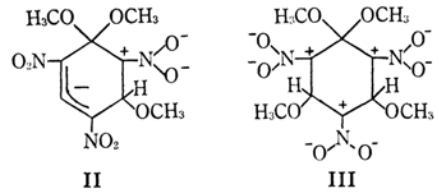

Fig. 1. Absorption spectra of 2, 4, 6-trinitroanisole ($2.15\times10^{-5}$ M) in methanol in the presence of sodium methoxide (path-length of cells, 1 cm.).
Concentrations of sodium methoxide:
1) $1.01\times10^{-2}$ M; 2) 1.23 M; 3) 2.46 M; 4) 3.94 M; 5) 4.92 M

1) R. Foster, *Nature*, **176**, 746 (1955); **183**, 1042 (1959).
2) V. Gold and C. H. Rochester, *J. Chem. Soc.*, **1964**, 1687.
3) T. Abe, This Bulletin, **37**, 508 (1964).
4) T. Abe, T. Kumai and H. Arai, ibid., **38**, 1526 (1965).

the measurements, because it took at least several minutes for the equilibrium needed for the formation of the first complex to be attained.[2,4] In the present wavelength region, 2, 4, 6-trinitroanisole at a low concentration and the methoxide ion did not absorb. The results are shown in Fig. 1.

Absorption curve 1, with two maxima at ca. 485 and 410 m$\mu$ for the solution at the methoxide concentration of $1.01\times10^{-2}$ M in Fig. 1, may be ascribed to the complex I.[1-4] The sbsorption intensity of the band at 410 m$\mu$ is stronger than that at 485 m$\mu$. When the concentration of the methoxide is increased, the absorption intensity of the band at ca. 480 m$\mu$ is stronger than that at ca. 410 m$\mu$ at the methoxide concentration of 3.94 M. From those results, the absorption maximum at 480 m$\mu$ in the curve 4 can be attributed to a second complex, one formed by a further reaction between the first complex I and the methoxide, as was suggested by Gold and Rochester.[2] They suggested that the second complex is likely to involve two methoxide ions per methyl picrate molecule. At the very much higher methoxide concentration of 4.92 M, the absorption intensity at ca. 480 m$\mu$ decreases and the absorption maximum at ca. 410 m$\mu$ disappears. This can be interpreted in terms of the formation of a third complex between the second complex and the methoxide, a complex with no absorption in the visible region. The above results lead to the conclusions that the Meisenheimer complex I has two bands, at ca. 485 and 410 m$\mu$; that the second complex has a band at ca. 480 m$\mu$, and that the third complex has no bands in the visible region.

Assuming that the second and the third complex are II and III respectively, the present author calculated the energy levels of the molecular orbitals of $\pi$-electrons in the three complexes I, II and III, using the same parameters as in the previous paper[3] by means of the simple LCAO MO method. The results are shown in Fig. 2. The predictions for the transitions in the complexes, indicated in Fig. 2, agree qualitatively with the experimental results in Fig. 1. Accordingly, it is likely that the second complex II with the absorption maximum at ca. 480 m$\mu$ and the third complex III with no absorption in the visible region are formed as the concentration of sodium methoxide increases.



II III

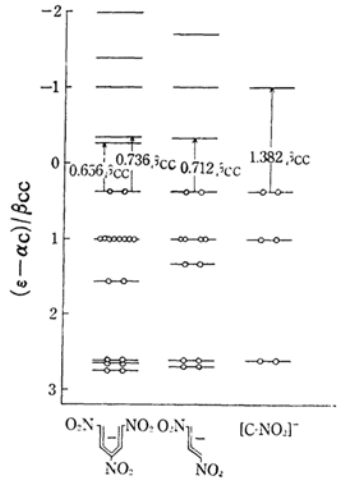



Fig. 2. The energy levels and transitions of $\pi$-electrons in the complexes I, II and III.