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INTERMEDIATES IN AROMATIC NUCLEOPHILIC SUBSTITUTION OF 4-METHOXY- AND 4-CHLORO-3,5-DINITROBENZOIC ACIDS WITH HYDROXIDE ION IN AQUEOUS DIMETHYL SULFOXIDE

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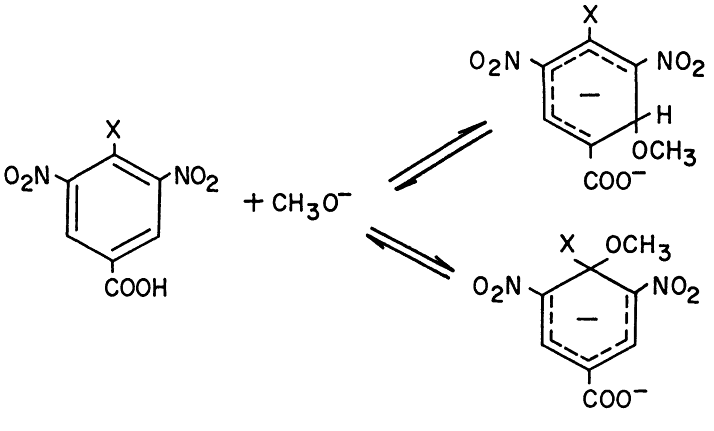
The reactions of 4-methoxy- and 4-chloro-3,5-dinitrobenzoic acids with hydroxide ion in aqueous dimethyl sulfoxide were studied by visible absorption spectroscopy. The formation of anionic σ-complexes, followed by intermediate complexes was observed.

A number of studies have been made on anionic σ-complexes1) produced in the nucleophilic substitution reactions of aromatic polynitrocompounds and hydroxide ion in solution. However, the formation of an intermediate complex has never been observed.2-8)

In this letter the spectral evidence for the formation of the intermediate complexes from 4-methoxy- and 4-chloro-3,5-dinitrobenzoic acids and hydroxide ion in aqueous dimethyl sulfoxide (DMSO) will be given. Spectral studies on the σ-complexes from 4-methoxy- and 4-chloro-3,5-dinitrobenzoic acids and methoxide ion will also be given.

Visible absorption spectra were recorded on a Hitachi RSP-2 Rapid Scan Spectrophotometer and a Hitachi 340 Spectrophotometer at room temperature. Pass length was 1.0 cm.

The visible absorption spectra observed 1/3 and 5 sec after mixing of sodium methoxide with 4-methoxy-3,5-dinitrobenzoic acid in methanolic DMSO are 1A and 1B in Fig. 1, respectively. The absorption band at 500 nm in curve 1A appeared at the initial stage is assignable to 1a.9) The spectrum 1B with the absorption maximum at 592 nm is attributable to 2a.9) The rapid scan spectrum from 4-chloro-3,5-dinitrobenzoic acid and sodium methoxide is 1C in Fig. 1, which is attributed to 1b. No evidence for the formation of 2b was obtained.



1 (a, X=OCH_3; b, X=Cl)

(1)

2 (a, X=OCH_3; b, X=Cl)

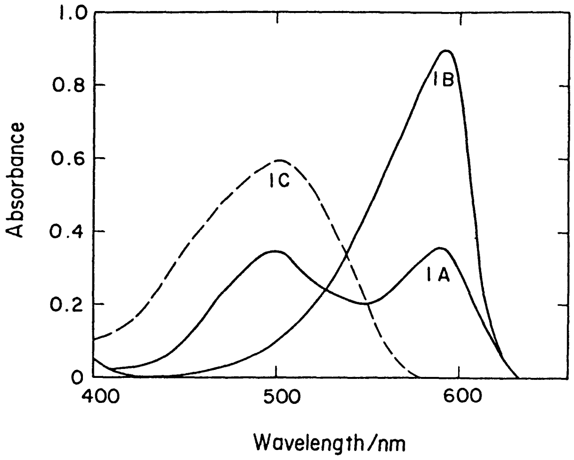
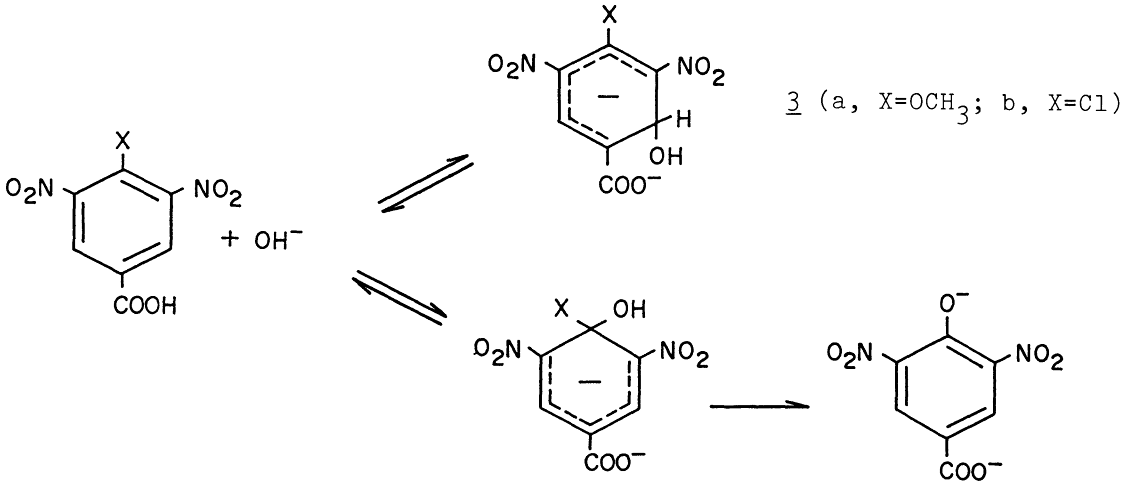


Fig. 1. The visible absorption spectra observed with the DMSO solution containing 4-methoxy-3,5-dinitrobenzoic acid (4.5×10^{-5} mol dm^{-3}), sodium methoxide (1.2×10^{-2} mol dm^{-3}) and methanol (2 % by volume); 1A and 1B, 1/3 and 5 sec after mixing respectively; 1C, the spectrum observed 25 msec after mixing of 4-chloro-3,5-dinitrobenzoic acid (1.5×10^{-3} mol dm^{-3}) with sodium methoxide (1.2×10^{-3} mol dm^{-3}) in methanolic DMSO (2 % methanol by volume).

Spectral changes relevant to the reaction of 4-methoxy-3,5-dinitrobenzoic acid with sodium hydroxide in aqueous DMSO are shown in Fig. 2. The absorption band at 500 nm appeared initially (curve 2A) may be attributed to the anionic σ-complex 3a by comparison with the band of 1a. The band at 595 nm in curve 2B may be assignable to the intermediate complex 4a. The final spectrum 2C with the absorption maximum at 475 nm is due to 5, because the same alkaline solution of 4-hydroxy-3,5-dinitrobenzoic acid in aqueous DMSO (2 % water by volume) showed the absorption band at 475 nm.



3 (a, X=OCH_3; b, X=Cl)

4 (a, X=OCH_3; b, X=Cl) 5

(2)

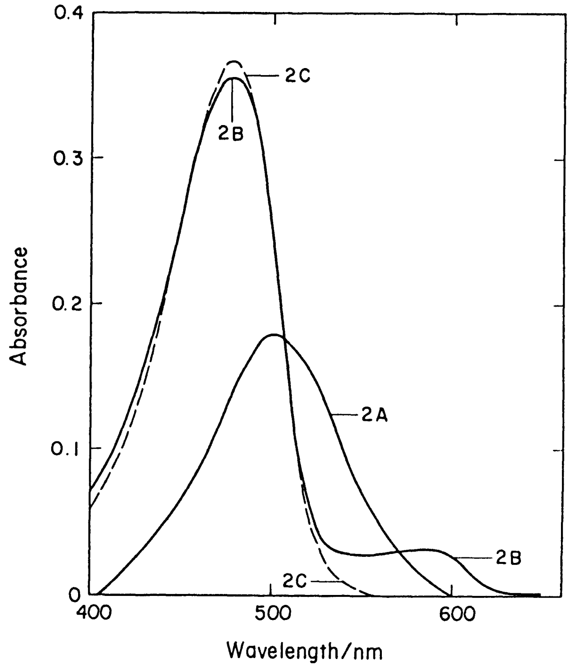


Fig. 2. The visible absorption spectra observed with the DMSO solution containing 4-methoxy-3,5-dinitrobenzoic acid (4.0×10^{-5} mol dm^{-3}), sodium hydroxide (2.3×10^{-3} mol dm^{-3}) and water (2 % by volume). Times measured after mixing: 2A, 10 sec; 2B, 3 min; 2C, 4h.

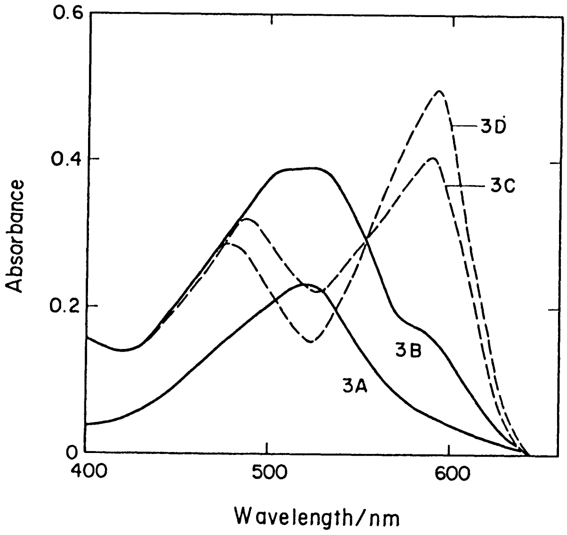


Fig. 3. The visible absorption spectra observed with the DMSO solution containing 4-chloro-3,5-dinitrobenzoic acid (4.7×10^{-5} mol dm^{-3}), sodium hydroxide (2.3×10^{-3} mol dm^{-3}) and water (2 % by volume). Times measured after mixing: 3A, 1/3 sec; 3B, 5 sec; 3C, 30 sec; 3D, 1 min.

Spectral changes relevant to the reaction of 4-chloro-3,5-dinitrobenzoic acid with sodium hydroxide are shown in Fig. 3. The absorption bands at 515 nm in curve 3A and 590 nm in curve 3D may be assignable to 3b and 4b, respectively. The spectrum obtained finally showed the absorption band at 475 nm, attributable to 5. The reaction scheme is given by eq. (2).

References

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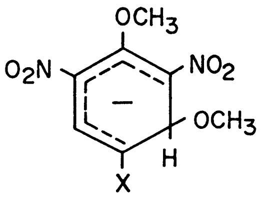
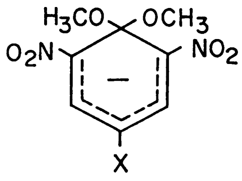
9) It is known that methoxide addition to 4-X-2,6-dinitroanisoles gives the kinetically favored 1,3-complexes like 6 and the thermodynamically stable 1,1-complexes like 7.[1,5,10,11] As regards their visible absorption spectra, for example, 6a, 6b, 7a and 7b show the absorption bands at 470, 480, 533 and 610 nm, respectively.[5,10,11]



6 (a, X=$COOCH_3$;
b, X=Cl)



7 (a, X=$COOCH_3$;
b, X=Cl)

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11) M. R. Crampton and H. A. Khan, J. Chem. Soc., Perkin Trans. 2, 1972, 1173.

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