

PHOTOREACTIONS OF AROMATIC COMPOUNDS X ^m
FLASH PHOTOLYSIS OF 3,5-DINITROANISOLE IN ALKALINE MEDIUM

J. Cornelisse and E. Havinga
Laboratory of Organic Chemistry
University of Leiden, Holland

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In an attempt to gain more information about the mechanism of nucleophilic photo-substitution reactions of aromatic nuclei (1,2,3), we have subjected a 1.2×10^{-4} M solution of 3,5-dinitroanisole in a mixture of methanol and 0.02 N aqueous NaOH (3.5 : 96.5) to flash photolysis ^{mm}. This system was chosen because irradiation of 3,5-dinitroanisole in this medium with continuous ultraviolet light yields 3,5-dinitrophenol in a clean reaction with quantum yield = 0.45 (4).

The flash apparatus was of the type described by Claesson and Lindqvist (5).

Use was made of a Joule flash (80 μ F, 7kV) with a duration (1/e time) of about 4 μ sec.

^m No. IX, J.L. Stratenus and E. Havinga, Rec. trav. chim. 85, ... (1966).

^{mm} The experiments were performed by means of flash photolysis apparatus of the "Laboratorium voor Fysische Chemie der Gemeentelijke Universiteit van Amsterdam".

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The events following the flash were studied by means of two techniques:

- a. Light from a second flash (10 μ F, 4kV), fired after a preset time interval was passed through the solution and dispersed by a Jarrell-Ash 1 m grating spectrograph onto Ilford HPS film.
- b. Light from a continuous source upon passing through the solution entered the spectrograph which now was used as a monochromator. The transmitted light at one chosen wavelength was focused on a photomultiplier tube directly coupled to an oscillograph. The oscillographtrace was photographed by means of a Polaroid Land camera.

From the spectrograph pictures obtained by the first technique it can be seen that upon the first flash (the photoflash), apart from 3,5-dinitrophenol, one or more products are formed which have an absorption in the region of 4250 - 5250 Å, probably extending towards longer wavelengths. The absorption diminishes gradually but persists for at least 40 msec (the largest interval employed in our experiments).

When after several minutes a photograph is taken by means of the spectroscopic flash alone, the intermediate absorption can no longer be detected and only some absorption below 4200 Å, due to the presence of the final product (3,5-dinitrophenolate), is observed.

Decay curves obtained by the second technique (wavelength of 520nm transmitted by the monochromator) were corrected for non-linearity of photomultiplier response. It seems probable that there are more than one intermediate absorbing at this wavelength. One of these has an estimated lifetime in the order of 10⁻¹ sec; for an other species a lifetime of several seconds seems to be a reasonable guess.

One of the intermediates is likely to be the σ -complex postulated to originate from the attack of hydroxide ion on the carbon atom bearing the CH₃O-group; also π -complexes may occur (2,3).

- 1) E. Havinga, R.O. de Jongh, W. Dorst, Rec. trav. chim. 75, 348 (1956) and following papers of this series.
- 2) R.O. de Jongh, Thesis, Leiden, 1965.
- 3) A review is given in: E. Havinga, Heterolytic photosubstitution reactions in aromatic compounds, 13th Solvay Congress of Chemistry, Brussels 1965.
- 4) E. Havinga and R.O. de Jongh, Bull. Soc. Chim. Belg. 71, 803 (1962).
- 5) S. Claesson and L. Lindqvist, Arkiv Kemi 12, 1 (1958).