Mechanism of the Conversion of a Nitrobenzene into a 4-Nitrosophenol in 15.8 M Potassium Hydroxide

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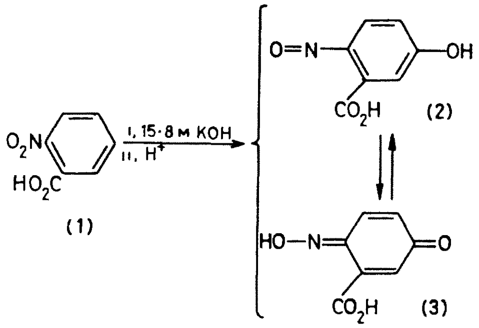
Summary Quantitative conversion of 2-nitrobenzoate ion into 2-nitroso-5-hydroxybenzoate ion occurs in 15·8 M potassium hydroxide; kinetic and spectral studies are consistent with a mechanism which involves rate-limiting formation of a Meisenheimer adduct with hydroxide ion followed by proton abstraction.

Formation of nitrosophenols from phenols by treatment with nitrosylating agents under acidic conditions[1] is sometimes unsuccessful.[2] We now report the first example of the use of 15·8 M KOH for the quantitative synthesis of the nitrosophenol derivative (**2**) [isolated as its quinone monoxime tautomer (**3**)] starting from the nitrobenzene derivative (**1**). In preparative-scale reactions, a heterogeneous mixture of 2-nitrobenzoic acid (20 g) in 400 ml of 15·8 M KOH was stirred at 60 °C under nitrogen for 20 h to give an insoluble salt of (**3**) (>15 g). The free acid (**3**) was obtained in two forms, (A) and (B), each of which was yellow. Form (A) crystallized when aqueous solutions of the salt were acidified with HCl and could be recrystallized from dioxane–light petroleum; form (A) had an i.r. spectrum [$\nu_{C=O}$ (KBr) 1723 cm^{-1} for –CO_2H] identical to that of (**3**) produced by photolysis of 2-nitro-5-hydroxybenzaldehyde.[2] Form (B) crystallized from acetone–light petroleum and had an i.r. spectrum very similar to that of form (A) but with a few significant differences (*e.g.*, $\nu_{C=O}$ 1704 cm^{-1}).†



A solution 15·8 M in potassium hydroxide has an H_- greater than 18,[3] and should therefore have a strong propensity to convert 2-nitrobenzoate ion (**4**) into the Meisenheimer complex[4] (**5**) and subsequently to abstract a proton from (**5**) to form (**6**). Loss of hydroxide ion from (**6**) gives rise to the product 2-nitroso-5-hydroxybenzoate ion (**7**). For reasons given below, formation of (**5**) is the rate-limiting step, with (**5**) and (**6**) present only at low concentrations.

The quinone monoxime (**3**) had a pK'_a of 6·45 at 25 °C, and the conjugate base had an absorption maximum at 404 nm with an ϵ_{max} which varied from 28,200 to 26,600

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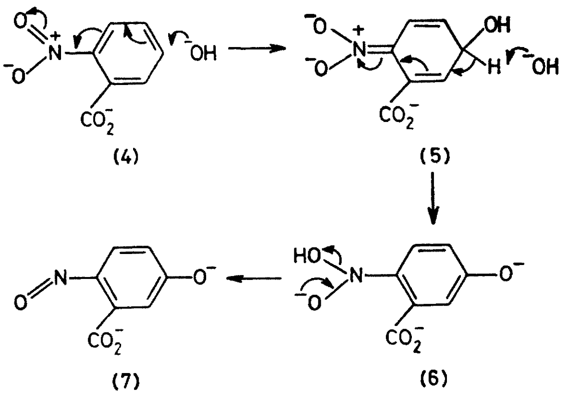
† Forms (A) and (B) both decompose between *ca.* 170 and 180 °C. They have identical mass spectra [*m/e* 167 ($M^{+\cdot}$, 60%), 153 (5%), 149 (100%)], identical ϵ_{max} values at 404 nm in 0·1 M NaOH (28,200 l mol^{-1} cm^{-1}, based on *M* 167·12) and identical elemental analyses corresponding to $C_7H_5NO_4$. Strong i.r. absorption peaks (N–O stretching) in form (A) (1023 cm^{-1}) and form (B) (1031 cm^{-1}) establish the quinone monoxime structure (**3**) (R. K. Norris and S. Sternhell, *Aust. J. Chem.*, 1966, **19**, 841; 1969, **22**, 935).



l mol^{-1} cm^{-1} over the entire range of alkalinity from pH 7 5 to 15·8 M KOH This established that the conjugate base of (**3**) did not undergo any significant amount of hydroxide-dependent modification in 15·8 M KOH In consideration both of the intensity and the wavelength of maximum absorption in comparison with those of other phenoxide ions,[5] the preponderant form of the conjugate base of (**3**) in 15·8 M KOH must be the resonance-stabilized nitroso species (**7**) and not the hydroxide adduct (**6**)

In dilute homogeneous solution at 25 °C, the initial u v spectrum of (**4**) in 15·8 M KOH‡ (λ_{max} 274 nm, ϵ_{max} 4640 l mol^{-1} cm^{-1}) is very similar to its spectrum in 10 M LiCl (λ_{max} 275 nm, ϵ_{max} 5900 l mol^{-1} cm^{-1}) and only slightly shifted from its spectrum at low ionic strength at pH 6·0 (λ_{max} 268 nm, ϵ_{max} 5300 l mol^{-1} cm^{-1}) These data establish that the 2-nitrobenzoate ion exists in 15·8 M KOH as the simple anion (**4**) and not as the Meisenheimer adduct (**5**)

The quantitative conversion of (**4**) at a concentration of 6×10^{-5} M, into (**7**), in 15·8 M KOH at 25 °C, has a half-life of 39 min and obeys a first-order rate law, with no precautions regarding oxygen During the course of the reaction, an isosbestic point occurs at *ca* 328 nm, indicating that the concentration of the intermediate (**5**) does not build up appreciably These data are consistent with the polar mechanism shown above with the conversion of (**4**) into (**5**) as the rate-limiting step Although alternative mechanisms involving free radical intermediates are possible,[6] such mechanisms are rendered unlikely by the quantitative formation of (**7**) in a kinetically simple reaction, even in the presence of oxygen §

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‡ Although a solution 15 8 M in KOH is supersaturated at 25 °C, it can remain homogeneous for several hours

§ Under the preparative conditions described earlier, nitrobenzene is largely unaltered owing to its low solubility in 15 8 M KOH A 3% yield of 4 nitrosophenol was obtained

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[6] G A Russell, E G Janzen, and E T Strom, *J Am Chem Soc* , 1964, **86**, 1807