Kinetics of the Reaction of *p*-Dinitrobenzene with Cyanide in Dimethylformamide

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The anion radical ($p\text{DNB}^-$) is formed in the reaction of *p*-dinitrobenzene (*p*DNB) with cyanide in dry and oxygen-free dimethylformamide (DMF). The rate of the radical formation was studied spectrophotometrically in the concentration range $10^{-4} \leq c_{p\text{DNB}} \leq 2 \times 10^{-3}$ mol dm^{-3} and $10^{-4} \leq c_{\text{CN}} \leq 10^{-2}$ mol dm^{-3}. The rate was first order in *p*-dinitrobenzene. For $c_{\text{CN}} > 10^{-3}$ mol dm^{-3} the reaction was also first order in CN^- with a second-order rate constant of $(3.65 \pm 1.2) \times 10^{-2}$ dm^3 mol^{-1} s^{-1}, an activation energy of (66 ± 7) kJ mol^{-1}, and an Arrhenius factor of 8.1×10^9 dm^3 mol^{-1} s^{-1} (0–40 °C). Radical formation is assumed to proceed *via* an intermediate Meisenheimer complex which reacts with a second cyanide ion to produce $p\text{DNB}^-$ and CN^-. The formation of the Meisenheimer complex is assumed to be rate determining.

Abe and Ikegami postulated that radical anions were the precursors to nucleophilic substitution reactions of dinitrobenzenes. They observed radical anions in the reactions of *o*-dinitrobenzene[1] and *p*-dinitrobenzene[2] with OH^- in aqueous dimethyl sulphoxide (DMSO). In dry and degassed DMF the *p*-dinitrobenzene anion radical ($p\text{DNB}^-$) was stable for several hours.[3] The behaviour of cyanide ion towards nitroaromatics has been recognized as being exceptional.[4] Whereas OH^- either replaces the substituent in the *para* position to the nitro group or replaces an H-atom in an *ortho* position, cyanide ion forms addition compounds (Meisenheimer complexes) with appropriately activated nitroaromatics.[5] Substitution reactions were only rarely observed. For instance, the reaction of KCN with *p*-dinitrobenzene in alcoholic solution yielded *p,p′*-dinitroazoxybenzene as well as *p*-nitroanisole or *p*-nitrophenetole in MeOH or EtOH, respectively. *p*-Nitrobenzonitrile or its hydrolysis products were not observed.[6] The kinetics of the nucleophilic substitution of the nitro group in *p*-dinitrobenzene have been studied for the reaction with RO^-,[7,8] OH^-,[2,8] and HO_2^-.[9]

Experimental

Materials.—DMF (Fluka ppa or Merck Uvasol) was dried over molecular sieves 4 Å [first statically and then dynamically over a column (*h* 150 cm, φ 3 cm)]. *p*DNB (Aldrich) was recrystallized from ethanol. *p*-Nitrophenol was obtained commercially (Merck), and *p*-nitrophenylhydroxylamine (Hy) was prepared according to the literature.[10] Tetrabutylammonium cyanide (Bu_4NCN) (Fluka) was recrystallized from toluene, dried at 40 °C under oil-pump vacuum, and kept in a dry argon or nitrogen atmosphere. The concentrations of stock solutions of Bu_4NCN were determined by titration with 0.01 mol dm^{-3} AgNO_3 with Dithizone as the indicator (0.01% in acetone).[11]

Techniques.—To remove oxygen, the freeze–pump–thaw technique was applied. The experiments were carried out in special cells (1 cm path length) where two solutions could be degassed separately before mixing. Before reaction the separated solutions were equilibrated to the reaction temperature. Immediately after mixing (≤20 s) the spectral changes were recorded on a Cary 14 or a Cary 2300 spectrophotometer.

Analysis of the absorption spectra. The concentration of the $p\text{DNB}^-$ radical anion was obtained from the absorbance at 800 nm (ε 1.10×10^4 dm^3 mol^{-1} cm^{-1}). The concentrations of the other reaction products were estimated by subtracting the spectra of the known components step by step from the reaction spectra. This procedure was applied only for a survey on the time dependence of the various reaction products. A detailed description is given in a supplementary publication.[†]

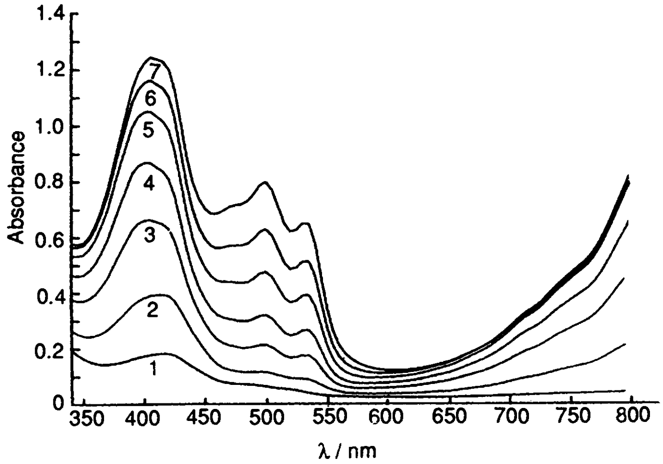

Figure 1. Absorbance change during the reaction of 1×10^{-4} mol dm^{-3} *p*DNB with 4.0×10^{-3} mol dm^{-3} Bu_4NCN in degassed DMF at 23 °C; spectra 1–7: 0, 10, 30, 50, 77, 102, and 132 min, respectively.

Results

Qualitative Observations.—*Spectral changes.* Addition of CN^- to degassed solutions of *p*DNB (10^{-4}–10^{-3} mol dm^{-3}) in DMF gave rise to several new bands in the absorption spectrum. Figure 1 shows the range 350–800 nm. The increase in absorbance at 800 nm was caused by the formation of a new band with a maximum at 920 nm. Two other new bands appeared, at 505 and 535 nm, having the same kinetics, and a band at *ca.* 400 nm changed its form and the position of its maximum during the course of the reaction. The absorption at 800 nm first increased and then declined slowly with a rate

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[†] Supplementary material has been deposited as Supplementary Publication No. SUP 56785 (15 pp) at the British Library Document Supply Centre. See 'Instructions for Authors (1990),' *J. Chem. Soc., Perkin Trans. 2*, p. xvii, in the January issue.

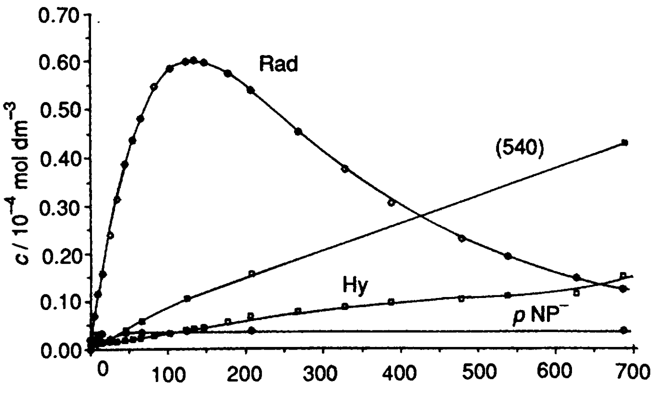

Figure 2. Product formation in the course of the reaction of 1.7×10^{-4} mol dm^{-3} pDNB with 2.5×10^{-3} mol dm^{-3} CN$^-$ in DMF: Rad: pDNB$^-$; (540): estimated concentrations of the product with absorptions at 505/540 nm, assuming ε 2×10^4 dm^3 mol^{-1} cm^{-1}.

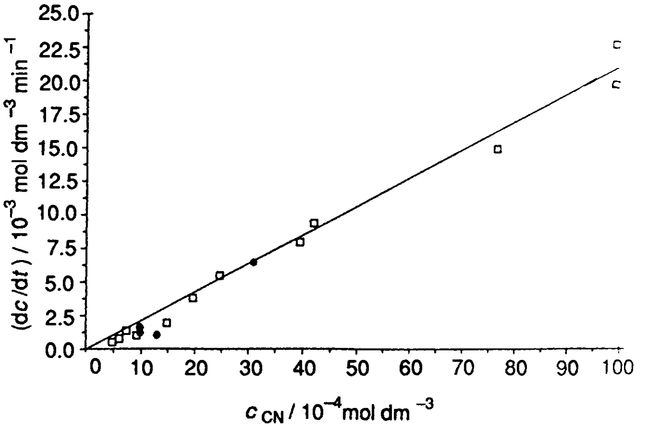

Figure 3. Initial rates of radical formation in DMF, normalized to 1 mol dm^{-3} pDNB, as a function of c_{CN}: □, 23 °C; ●, 20 °C.

depending on the cyanide concentration. The 400 nm band appeared immediately (≤ 20 s) after mixing. At the start, its maximum was at 430 nm. During the reaction it was blue shifted concurrently with the increase at 800 nm. When the latter declined the shift was reversed. However, the maximum remained at $\lambda < 430$ nm. On exposure of the sample to air, the 800 nm band disappeared within 5 min. The twin bands 505/535 nm decreased more slowly than the absorption at 800 nm. It took more than 30 min for these two bands to disappear completely. A shoulder at the long-wavelength side of the 400 nm band remained and was due to a broad band with a maximum at *ca.* 510 nm.

Identification of the reaction products. The absorption > 800 nm is assigned to the radical anion pDNB$^-$. We were able to prepare the radical anion in DMF electrochemically and to obtain the molar absorptivity coefficients.[3] The change in shape of the 400 nm band (Figure 1) is caused by the contribution of the radical anion absorption at 400 nm. The ESR spectrum obtained from a degassed solution of pDNB and CN$^-$ in DMF was identical with that in the literature.[12]

The second component that contributed to the absorption at *ca.* 400 nm was the p-nitrophenoxide ion (pNP$^-$). pNP$^-$ has been established as the main product of the reaction of pDNB with OH$^-$.[13] In the presence of excess of CN$^-$ p-nitrophenol is quantitatively deprotonated; only the bands of pNP$^-$ were present in those solutions [λ_{max} 432 nm (ε_{max} 3.7×10^4 dm^3 mol^{-1} cm^{-1})].

p-Nitrophenylhydroxylamine (Hy) is the first stable reduction product of pDNB in aqueous solution.[14] In DMF, (Hy) is thermally stable [λ_{max}(DMF) 378 nm (ε 1.4×10^4 dm^3 mol^{-1} cm^{-1})]. Spectra of solutions of pDNB and Hy show only the superposition of the spectra of the components. However, Hy is less stable if the solution is alkaline,[15] as well as in the presence of cyanide. In alkaline solutions Hy is deprotonated, producing new bands in the absorption spectrum at 480 nm. At 5 °C the decomposition was sufficiently slow to allow us to extrapolate a series of absorption spectra to zero time and so to obtain the spectrum of the base form [λ_{max}(DMF) 465 nm (ε 1.7×10^4 dm^3 mol^{-1} cm^{-1}), 485 (1.7×10^4), and 520 sh]. The acid–base equilibrium is such that in the presence of cyanide (10^{-5}–10^{-3} mol dm^{-3}) both forms are present in comparable concentrations. The base form, however, formed a stable adduct with pDNB [λ_{max}(DMF) 505 nm (ε 2.1×10^4 dm^3 mol^{-1} cm^{-1})]. Adduct formation was quantitative after 20 min. When mixtures of pDNB and CN$^-$ had reacted for longer than 20 min, Hy was present only as the adduct, whereas initially both forms could be identified from the absorption spectra (see the supplementary publication).

The twin maxima at 505/535 nm have not yet been assigned. They only appeared when CN$^-$ was present. On account of their air sensitivity we assume that they are due to a radical species. Although being rather conspicuous, they only contributed to a fraction of the absorption because the greater part was due to the superimposed absorption of Hy. Assuming an absorptivity ε of 2×10^4 we estimate* that not more than 5% of this unknown product had been formed in the initial phase of the radical formation. Figure 2 shows an estimate of how the concentrations of the various products developed over a period of time. While the radical concentration could be unambiguously determined from the absorbance at 800 nm, the other components of the reaction mixture had to be evaluated by a complicated spectral analysis, where at least one compound was unknown. Therefore large experimental errors will be involved in this procedure. However, we believe that the time dependence is basically correct. The formation of radical anion was linear in the first 20–30 min. The pDNB$^-$ concentration peaked and finally declined exponentially. In the experiment reported in Figure 2 the maximum radical anion concentration corresponded to 36% conversion of the initial pDNB. p-Nitrophenol was formed only initially, probably by reaction of pDNB with OH$^-$ which originated from traces of water in the solvent. The concentrations of Hy and the unknown product increased beyond the maximum of the radical anion concentration.

Quantitative Factors.—Kinetics of radical formation. The radical anion was the main observable product in the reaction of pDNB and CN$^-$. We obtained radical anion yields of $\leq 60\%$. At $T \leq 30$ °C, the radical anion concentration increased linearly with time in the first 20 min. Hence the reaction rate could be obtained from the initial slope. Figure 3 presents the initial rates as functions of the pDNB and CN$^-$ concentration. In 1.66×10^{-4} mol dm^{-3} pDNB and $c_{CN} \geq 10^{-3}$ mol dm^{-3} the reaction was first order in both pDNB and cyanide. The second-order rate constant k', $(3.65 \pm 0.12) \times 10^{-2}$ dm^3 mol^{-1} s^{-1}, was obtained from the initial slopes at 23 °C. Estimating the pDNB consumption from the formation of the radical anion—thus neglecting formation of the other products—we found that pDNB disappearance was exponential under our experimental conditions (excess of CN$^-$), with $k_{-pDNB}/c_{CN} = (3.3 \pm 0.2) \times 10^{-2}$ dm^3 mol^{-1} s^{-1}. This value is somewhat smaller than k', in agreement with the underestimation of the pDNB consumption.

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* All the other species involved have absorptivities between 1×10^4 and 4×10^4 dm^3 mol^{-1} cm^{-1}. A value of 2×10^4 seems, therefore, to be reasonable.

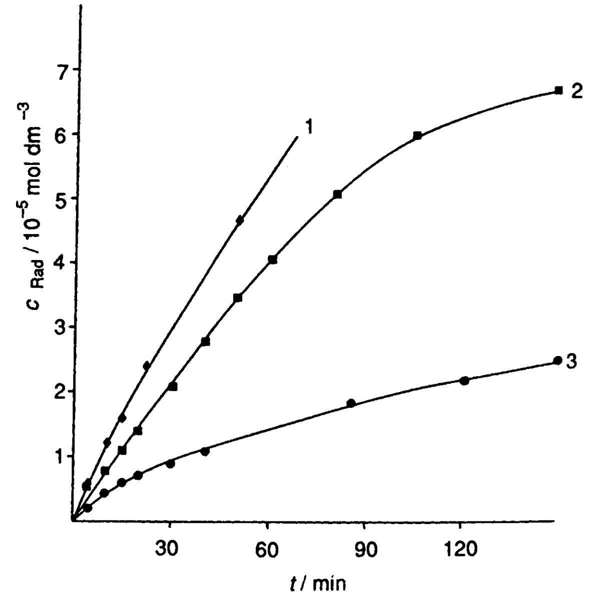


Figure 4. Effect of water on the reaction of 8 × 10^{-4} mol dm^{-3} pDNB and 1 × 10^{-3} mol dm^{-3} CN$^-$ in DMF at 20 °C; (1) ≤0.006%; (2) 0.15%; (3) 2% water.

On reduction of the cyanide concentration below 10^{-3} mol dm^{-3}, the apparent second-order rate constant decreased. Below 2 × 10^{-4} mol dm^{-3} we did not observe the radical anion. Figure 3 shows that the data points lie below the straight line for low CN$^-$ concentrations.

The temperature dependence of the radical formation (0–40 °C) yielded an activation energy, E_a of 66 ± 7 kJ mol^{-1} and an Arrhenius factor, A, of 8.1 × 10^9 dm^3 mol^{-1} s^{-1}. For a second-order reaction, these values are related to the enthalpy and entropy of activation by equation (1),[16] which gives, for T 293 K: $\Delta H^\ddagger$ 61 kJ mol^{-1} and $\Delta S^\ddagger$ −71 J mol^{-1} K^{-1}.

$$\Delta H^\ddagger = E_a - 2RT; \Delta S^\ddagger = 2.3R(\log A - \log T - 11.18) \quad (1)$$

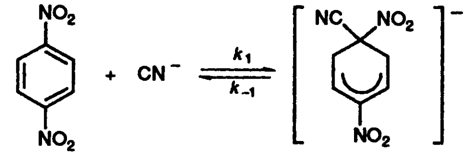
Effects of additives. Addition of the stable reaction products p-nitrophenol and Hy did not influence formation of the radical anion. The reaction was, however, sensitive to water. Three different preparation concentrations were compared: (1) DMF dried with molecular sieves 4 Å (≤0.006% water), (2) DMF (Merck, Uvasol) used as supplied (≤0.15% water as specified by the manufacturer), and (3) DMF with 2% water added. Figure 4 shows the effect on formation of the radical anion. The reaction rate was reduced and the amount of phenoxide produced was enhanced. The kinetics in DMF containing water are clearly affected by side reactions of pDNB with hydroxide ion[2] formed in the presence of CN$^-$.

Radical decay. The radical decay was also pseudo-first-order under our experimental conditions. The decay was exponential after *ca.* twice the time needed to reach absorption maximum. A second-order rate constant of (1.4 ± 0.2) × 10^{-2} dm^3 mol^{-1} s^{-1} was obtained from these data. The radical concentration decreased more rapidly than the rate at which Hy was formed. The unknown product with maxima at 505/540 nm increased further after the radical anion had disappeared (Figure 2).

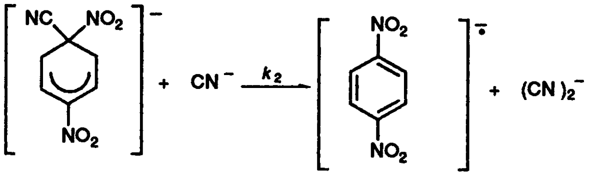
Discussion

The anion radical of pDNB is the main product when pDNB reacts with cyanide ion in DMF. pNP$^-$ is produced only if water is present. Hydroxide ion formed from water with CN$^-$ reacts in a nucleophilic substitution reaction to afford pNP$^-$.[2] Hy is formed in a secondary reaction from the pDNB$^-$ radical anion.[3]

The rate law for formation of the radical anion is first order both in pDNB and in CN$^-$. Direct reduction by cyanide, however, is unfeasible. Eberson[17] demonstrated that OH$^-$ is not likely to reduce pDNB directly. Taking into account the fact that CN$^-$ has a more positive normal potential than does OH$^-$ (*e.g.*, 1.9 V and 2.59 V in water[18] and 0.8 and 1.1 V in acetonitrile[17] for OH$^-$ and CN$^-$, respectively), reduction by cyanide is even less feasible. On this basis we propose the following mechanism as shown by equations (2) and (3). pDNB reacts with CN$^-$ to form a σ-bonded intermediate



(2)



(3)

(Meisenheimer complex) that reacts with a second cyanide ion to produce the radical anion and (CN)$_2^-$. The cyanogen ion radical has been detected by ESR spectroscopy in γ-irradiated sodium cyanide[19] and by pulse radiolysis of aq. cyanogen solutions, where it had a half-life of 2 μs.[20]

Assuming steady-state conditions, the rate of formation of the radical anion is given by equation (4). For $c_{\mathrm{CN}} \gg k_{-1}/k_2$ the rate

$$\frac{dc_{\mathrm{R}}}{dt} = k_2 c_\sigma c_{\mathrm{CN}} = \frac{k_1 c_{p\mathrm{DNB}} c_{\mathrm{CN}}^2}{\dfrac{k_{-1}}{k_2} + c_{\mathrm{CN}}} \quad (4)$$

is first order in c_{CN}. For $c_{\mathrm{CN}} \ll k_{-1}/k_2$ a rate law second order in c_{CN} would be expected. The decrease in the apparent first-order rate constant that we observed at low CN$^-$ concentrations could be caused by this effect. For lower CN$^-$ concentrations no formation of radical anion could be detected. On the other hand CN$^-$ consumption by some impurities in the solvent cannot be excluded. According to the proposed mechanism, k_1, the rate of formation of the Meisenheimer complex, is rate determining at high CN$^-$ concentrations. The order of magnitude of k_1 is as expected for formation of the σ-complex. For example, formation of the more stable Meisenheimer complex of trinitrobenzene and CN$^-$ proceeds in chloroform with a rate of 2.25 × 10^2 dm^3 mol^{-1} s^{-1} at 25 °C,[5] whereas the self-exchange reaction $p\mathrm{DNB} + p\mathrm{DNB}^- \longrightarrow p\mathrm{DNB}^- + p\mathrm{DNB}$ has a rate constant[21] of 6 × 10^8 dm^3 mol^{-1} s^{-1}. The substitution of the nitro group in pDNB by EtO$^-$ in EtOH has a rate constant[8] of 2 × 10^{-3} dm^3 mol^{-1} s^{-1} (25 °C). 1,2-Dinitrobenzenes[22] undergo substitution reactions with rates of an order of magnitude of 10^{-4} dm^3 mol^{-1} s^{-1}. These values are significantly smaller than k_1. It seems that in those substitution reactions the dissociation of the nitrite is the rate-determining step.

The activation parameters are also in agreement with the formation of a Meisenheimer complex. The formation of nitroanisole–MeO$^-$ complexes has activation energies in the range from 24–75 kJ mol^{-1} and negative activation entropies.[4b] A negative entropy of activation is to be expected for adduct formation where one of the components is uncharged.

The slow formation of the radical anion pDNB$^-$ suggests $k_2 \gg k_1$. In this case we do not expect that the steady-state concentration of the Meisenheimer complex will be sufficient for spectroscopic detection.

pNP$^-$ was not produced during radical decay in our experiments. The radical is obviously not the precursor in the nucleophilic substitution of pDNB.

Acknowledgements

Financial assistance of the *Deutsche Forschungsgemeinschaft* and the *Verband der Chemischen Industrie* is gratefully acknowledged. We thank Priv. Doz. Dr Grampp, Erlangen, for recording the ESR spectra and Miss Lynne Coppillie for critically reading the manuscript.

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Paper 9/03136G
Received 25*th July* 1989
Accepted 27*th March* 1990