# Bromopicrin Reaction. Part II.[1] Reaction between 2-Nitroethanol and Sodium Hypobromite

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Reaction between 2-nitroethanol and sodium hypobromite gives bromopicrin ($CBr_3NO_2$) in high yield. A kinetic study indicates that 2,2-dibromo-2-nitroethanol is an intermediate and that the rate-determining step is proton removal from 2-nitroethanol.

Reaction of picric acid and an alkaline solution of sodium hypobromite results in complete breakdown of the benzene ring and one product of the reaction is bromopicrin. In Part I [1] the initial step in this reaction was shown to be attack of hypobromite on a 1 : 1 adduct of picrate and hydroxide ions to give a ring-opened product. A number of steps must then follow before formation of bromopicrin and this multitude of steps makes elucidation of the reaction mechanism difficult. For this reason we examined a much simpler, but related, system in the hope that it might throw some light on the mechanism of the bromopicrin reaction. The reaction between sodium hypobromite and 2-nitroethanol was chosen for this purpose.

Addition of 2-nitroethanol to sodium hypobromite solution results in the evolution of heat and the rapid formation of bromopicrin, which separates as a heavy oil. This result is entirely consistent with the suggestion, made in Part I, that hydroxy-nitro-compounds are intermediates in the conversion of picric acid to bromopicrin. The mechanism of the alkaline bromination of nitromethane (which yields bromopicrin if sufficient bromine is present [2]) is well known [3] and we can suggest, as a working hypothesis, a similar mechanism for the reaction of 2-nitroethanol and sodium hypobromite. A proton $\alpha$ to the nitro-group is removed by hydroxide ion and the resulting anion reacts with bromine to give 2-bromo-2-nitroethanol. This process is repeated to

$$HOCH_2CH_2NO_2 \xrightarrow{OH^-} HOCH_2\bar{C}HNO_2 \xrightarrow{Br_2} HOCH_2CHBrNO_2 + Br^-$$

$$HOCH_2CHBrNO_2 \xrightarrow{OH^-} HOCH_2\bar{C}BrNO_2 \xrightarrow{Br_2} HOCH_2CBr_2NO_2 + Br^-$$

$$HOCH_2CBr_2NO_2 \xrightarrow{Br_2\text{-}OH^-} CBr_3NO_2$$

SCHEME 1

give 2,2-dibromo-2-nitroethanol (see Scheme 1). Further bromination of this compound to give bromopicrin will be discussed later. Some support for this reaction scheme comes from the observation that the n.m.r. spectrum of nitroethanol, after treatment with sodium

[1] Part I, A. R. Butler and H. F. Wallace, *J. Chem. Soc.* (*B*), 1970, 1758.

[2] M. V. Meyer and J. Tscherniak, *Annalen*, 1876, **180**, 122.

[3] A. Hantzsch and A. Veit, *Ber.*, 1899, **32**, 607.

deuterioxide in $D_2O$, showed complete replacement of the methylene protons α to the nitro-group, indicating their acidic nature. Also, 2-bromo-2-nitroethanol reacts readily with alkaline sodium hypobromite to give bromopicrin, which is consistent with its intermediacy

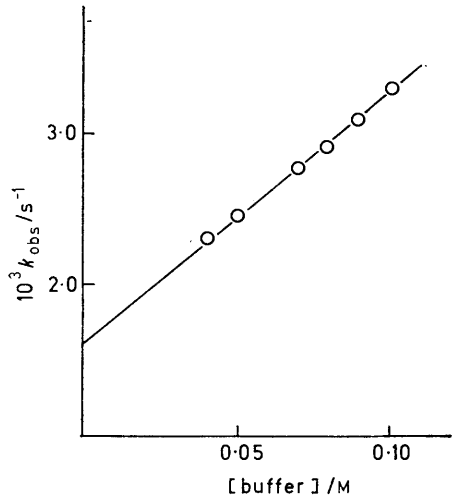



FIGURE 1 Variation of $k_{obs}$ with buffer concentration (pH 9·01) for the ionisation of 2-nitroethanol at 25°

in Scheme 1. In our mechanistic study of the formation of bromopicrin from nitroethanol we examined first the ionisation of nitroethanol.

Addition of alkali to an aqueous solution of 2-nitroethanol results in the appearance of an absorption peak with a maximum at 237 nm, which we ascribe to the anion $HOCH_2\bar{C}HNO_2$. By monitoring the appearance of this peak the rate of ionisation in a borax buffer (pH = 9·01) was measured. The ionisation was studied as a function of buffer concentration at a constant ionic strength (0·1M) and the results are shown in Figure 1. Extrapolation to zero buffer concentration gives the value of $k_2$ for transfer of a proton from nitroethanol to hydroxide ion as $1{\cdot}65 \times 10^2$ l mol$^{-1}$ s$^{-1}$. Examination of the data in Figure 1 indicates the surprisingly large effect the buffer concentration has on the rate of ionisation where one might have imagined that the rate would have been determined principally by the hydroxide ion concentration. An anomalously low rate of reaction between hydroxide ion and carbon acids has been noted by other authors.[4] We have suggested that the slow step in the bromination of nitroethanol is this initial ionisation but before presenting evidence to confirm this it is necessary to examine the stoicheiometry of the reaction.

Hypobromite ion has an absorption peak [5] at 330 nm (ε 301) and its disappearance can be followed spectrophotometrically. Addition of a known quantity of nitroethanol to sodium hypobromite solution results in the rapid consumption of *ca.* three moles of hypobromite for every mole of nitroethanol added. This is followed by the slow disappearance of more hypobromite. The initial reaction is entirely consistent with the mechanism shown in Scheme 1 and the further consumption of hypobromite is probably due to reaction with formaldehyde formed, along with bromopicrin, as a result of the final step in the reaction. Qualitative spectral studies with hypobromite and formaldehyde present at concentrations comparable with those occurring after formation of bromopicrin indicate that this is a reasonable explanation. This reaction was not investigated further.

More insight can be gained by scanning the spectrum of the reaction mixture over the range 230—400 nm at timed intervals. In a buffer of pH 8·61 (0·1M and containing $5{\cdot}12 \times 10^{-3}$M-bromine) the decrease in absorption at 330 nm, due to consumption of hypobromite, is paralleled by an increase in absorption at 250 nm due to formation of bromopicrin (the spectrum of which had been determined separately). During this part of the reaction there is a tight isosbestic point at 275 nm and the spectral changes at 250 and 330 nm are consistent with complete conversion of the nitroethanol into bromopicrin (Figure 2). The single isosbestic point indicates that there is only one slow step in the reaction and the most likely one is the first, *i.e.* ionisation of nitroethanol. More direct evidence for this is given below. After *ca.* 20 min the isosbestic point is lost as the reaction between formaldehyde and hypobromite becomes more important. This is *ca.* four half-lives of the reaction leading to the formation of bromopicrin (see below) and shows how the approximately correct stoicheiometry for the consumption of hypobromite is observed but why no infinity reading of the optical density at 330 nm can be obtained.

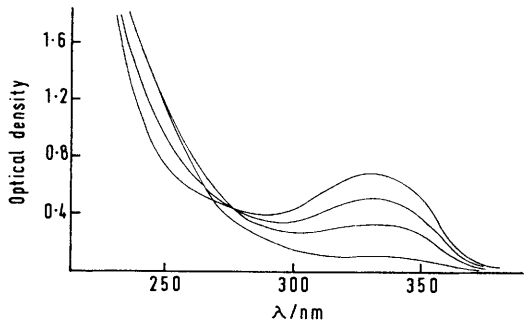



FIGURE 2 Spectral changes occurring after *ca.* 1, 4, 13, and 45 min during the reaction of 2-nitroethanol and sodium hypobromite in a borax buffer (pH 8·61): $[\text{nitroethanol}]_0 = 9{\cdot}6 \times 10^{-4}$M; $[Br_2]_0 = 5{\cdot}1 \times 10^{-3}$M

The spectral studies described above are unsuitable for the precise determination of rate constants as the cuvette containing the reaction mixture was not adequately thermostatted. Therefore, we measured the variation of optical density with time at 250 and 330 nm (corresponding to bromopicrin formation and hypobromite consumption) in two separate experiments by the use of a single beam spectrophotometer with the cuvette thermostatted at 25°. The results of one pair of runs are shown in the Table. The variation of optical density with time at 250 nm shows that bromopicrin

[4] Z. Margolin and F. A. Long, *J. Amer. Chem. Soc.*, 1972, **94**, 5108.

[5] L. Farkas and F. S. Kelin, *J. Chem. Phys.*, 1948, **16**, 886.

formation is of the first order with a rate constant of $2{\cdot}8\ (\pm 0{\cdot}2) \times 10^{-3}\ s^{-1}$. It is more difficult to determine the rate constant for the consumption of hypobromite as no infinity reading can be taken because of the subsequent reaction with formaldehyde. From the spectral studies described above it is clear that this reaction

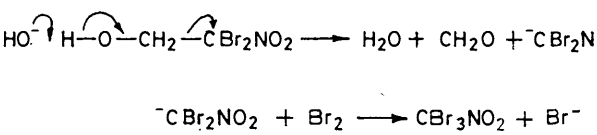
Optical density changes during the reaction between 2-nitroethanol [a] and sodium hypobromite [b] at pH 8·61

| $t$/min | 330 nm | 250 nm | 237 nm [c] |
|---|---|---|---|
| 0 | 0·690 | 0·610 | 0·120 |
| 2 | 0·590 | 0·717 | 0·202 |
| 4 | 0·515 | 0·803 | 0·255 |
| 6 | 0·462 | 0·855 | 0·293 |
| 8 | 0·420 | 0·891 | 0·322 |
| 10 | 0·388 | 0·923 | 0·343 |
| 12 | 0·368 | 0·955 | 0·357 |
| 14 | 0·352 | 0·969 | 0·367 |
| 16 | 0·338 | 0·976 | 0·373 |
| 18 | 0·326 | 0·981 | 0·380 |
| 20 | 0·315 | 0·983 | 0·384 |
| 22 | 0·308 | 0·984 | 0·387 |
| 24 | 0·300 | 0·986 | 0·390 |
| 26 | 0·293 | 0·988 | 0·392 |
| 45 | 0·205 | 0·992 | 0·400 |

[a] $8{\cdot}6 \times 10^{-4}$M. [b] $[Br_2]_0 = 5{\cdot}1 \times 10^{-3}$M. [c] Ionisation of 2-nitroethanol, no bromine present.

becomes significant after *ca.* 20 min and this is sufficient time to permit the application of Guggenheim's method [6] for the determination of the rate constant. This indicates that hypobromite is consumed in a reaction of the first order with a rate constant of $2{\cdot}3\ (\pm 0{\cdot}3) \times 10^{-3}\ s^{-1}$. This is in reasonable agreement (in view of the experimental difficulties) with that obtained for the formation of bromopicrin. Therefore, consumption of hypobromite and bromopicrin formation occur at the same rate. The rate of ionisation of 2-nitroethanol in the same buffer was then determined (see Table). The value obtained was $2{\cdot}6\ (\pm 0{\cdot}1) \times 10^{-3}\ s^{-1}$, which is the same as that for the loss of hypobromite and the formation of bromopicrin. Thus, the rate-determining step in this reaction is the first ionisation. Attack of bromine, the second ionisation, and fission of the carbon–carbon bond are all faster and a simple kinetic study of the reaction yields no further information about these steps.

Bromination of 2-nitroethanol in the presence of a base to give 2,2-dibromo-2-nitroethanol is not an unexpected reaction but the fission of the carbon–carbon bond in this molecule, and the subsequent reaction with bromine to give bromopicrin, pose several problems. In the related reaction between hypobromite and nitroethane bromination stops once the dibromo-compound ($CH_3CBr_2NO_2$) has formed, suggesting that the hydroxy-group is necessary for cleavage to occur. A compound more similar to 2-nitroethanol, but without a hydroxy-group, is methyl 2-nitroethyl ether ($MeOCH_2CH_2NO_2$). Reaction of this compound with sodium hypobromite gave 2,2-dibromo-2-nitroethyl methyl ether but again this molecule showed no tendency to cleave. This suggests that the fission of the 2,2-dibromo-2-nitroethanol molecule in an alkaline medium involves attack at the hydroxy-group and concerted expulsion of the $^-CBr_2NO_2$ ion (Scheme 2). A study of the leaving



SCHEME 2

tendency of the $^-CBr_2NO_2$ anion is reported in the following paper.

At first sight the final step in the formation of bromopicrin is reaction between the $^-CBr_2NO_2$ ion and bromine but the situation may be more complex than this. In the alkaline bromination of bromoform to give tetrabromomethane Bell and Ford-Smith [7] have shown that it is not the anion $^-CBr_3$ which reacts with bromine, but a bromide ion is lost from this species and bromine reacts with the resulting dibromocarbene to give tetrabromomethane. There is some evidence that $^-CBr_2NO_2$ may give rise to a carbene. Trénel and Wilkendorf [8] report that the reaction of 2,2-dibromo-2-nitroethanol with sodium hydroxide results in the vigorous evolution of carbon monoxide and precipitation of potassium bromide. This is typical of the hydrolysis of a carbene.[9] Therefore, it may be that the anion $^-CBr_2NO_2$ loses bromide ion to give bromonitrocarbene and it is this species which reacts with bromine to give bromopicrin. It is impossible to trap a carbene by addition across a double bond in the presence of bromine and so investigation of this part of the reaction is difficult, and no direct evidence for carbene formation has been obtained.

The fission of 2,2-dibromo-2-nitroethanol into formaldehyde and the $^-CBr_2NO_2$ anion is the reverse of the type of aldol condensation used to prepare 2-nitroethanol (the reaction of formaldehyde and nitromethane in the presence of a base). With two bromine atoms present it appears that the anion is stabilised to such an extent that the reverse reaction is preferred and reaction of the anion with bromine leads to the irreversible formation of bromopicrin.

## EXPERIMENTAL

N.m.r. spectra were recorded for solutions in $D_2O$ or carbon tetrachloride.

2-Nitroethanol was prepared by the reaction between paraformaldehyde and nitromethane,[10] $\tau$ 5·7 (m) and 6·2 (m). Treatment with sodium deuterioxide and subsequent acidification with deuteriosulphuric acid completely removed the multiplet at $\tau$ 5·7 and left a singlet at $\tau$ 6·2. Solution in 0·1M-sodium hydroxide gave the anion, $\lambda_{max.}$ 237 nm ($\varepsilon$ $1{\cdot}9 \times 10^5$). 2-Bromo-2-nitroethanol was prepared by the action of bromine on the sodium salt of 2-nitroethanol,[11] $\tau$ 5·8 (d) and 3·9 (t) (the downfield shift is due to the inductive effect

[6] E. A. Guggenheim, *Phil. Mag.*, 1926, **2**, 538.
[7] R. P. Bell and M. H. Ford-Smith, *J. Chem. Soc.*, 1961, 1413.
[8] M. Trénel and R. Wilkendorf, *Ber.*, 1924, **17**, 2126.
[9] J. Hine, *J. Amer. Chem. Soc.*, 1950, **72**, 2438; E. A. Robinson, *J. Chem. Soc.*, 1961, 1663.
[10] W. E. Noland, *Org. Synth.*, 1961, **41**, 67.
[11] M. H. Gold, E. E. Hamel, and K. Klager, *J. Org. Chem.*, 1957, **22**, 1665.

of the bromine). 2-Chloroethyl methyl ether was obtained by methylation of chlorohydrin with dimethyl sulphate,[12] and converted to the corresponding iodo-compound by refluxing with sodium iodide in acetone.[13]

*Methyl 2-Nitroethyl Ether.*—2-Iodoethyl methyl ether (18 g) was refluxed with silver nitrite (18 g) for 3 h in dry ether (100 ml). After filtration the ether was removed to leave an *oil*, b.p. 85° at 15 mmHg (34%) (Found: C, 34·54; H, 6·75; N, 12·54. $C_3H_7NO_3$ requires C, 34·3; H, 6·7; N, 13·3%), $\nu_{max.}$ 1550 and 1370 $cm^{-1}$, $\tau$ 6·7 (s), 6·2 (t), and 5·6 (t).

Bromopicrin was prepared by a method of Hunter.[14]

*Reactions with Sodium Hypobromite.*—(a) *2-Nitroethanol.* Addition of 2-nitroethane to sodium hypobromite resulted in formation of a heavy oil, which was extracted with ether and identified as bromopicrin by elemental analysis and i.r.

(b) *Nitroethane.* A mixture of nitroethane and an excess of sodium hypobromite was stirred for 3 h. The resulting oil was extracted with ether, distilled, and identified as 1,1-dibromo-1-nitroethane by elemental analysis and i.r. and n.m.r. spectroscopy.

(c) *Methyl 2-nitroethyl ether.* The above reaction was repeated and *2,2-dibromo-2-nitroethyl methyl ether* was obtained as a yellow *oil*, b.p. 110° at 15 mmHg (45%) (Found: C, 13·6; H, 2·1; N, 4·9. $C_3H_3NO_3Br_2$ requires C, 13·7; H, 1·9; N, 5·3%).

*Spectral Studies.*—A solution of 2-nitroethanol in dioxan (0·19M, 0·05 ml) was added to a mixture of borax buffer (9 ml) and bromine solution ($5{\cdot}12 \times 10^{-2}$M, 1 ml) and the spectra were recorded on a Unicam SP 800 spectrophotometer at timed intervals during 45 min. The pH of the mixture was 8·61 (Beckman Research pH meter).

*Kinetic Studies.*—The above experiment was repeated with all the solutions thermostatted at 25° and the variation of absorbance with time was followed on a Unicam SP 500 spectrophotometer. A similar method was used to measure the rate of ionisation of 2-nitroethanol in a borax buffer. The ionic strength was kept at 0·1M by addition of KCl.

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[12] L. C. Swallen and C. E. Board, *J. Amer. Chem. Soc.*, 1930, **52**, 651.

[13] K. Kurasawa, H. Obara, and H. Uda, *Bull. Chem. Soc. Japan*, 1966, **39**, 530.

[14] L. Hunter, *J. Chem. Soc.*, 1923, **123**, 543.