# The Reaction of Bromine with Cyclohexene in Carbon Tetrachloride. Part 1. Reactions in the Absence of Hydrogen Bromide; Presence of a Scavenger [1]

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The addition of bromine to cyclohexene in carbon tetrachloride solutions has been studied. Results are unreproducible, but when *N*-bromosuccinimide or *N*-bromophthalimide is also present to scavenge hydrogen bromide, a slower reaction, second-order in bromine, with reproducible rate constants is observed. This shows a negative overall activation energy. There may be terms in higher powers of [$Br_2$], but the first-order term in bromine is too small to measure. A faster second phase of the reaction begins when all the *N*-bromo-imide initially present has reacted with the hydrogen bromide formed in side reactions, including those leading to 3-bromocyclohexene and (from adventitious water) to 2-bromocyclohexanol, and is of order 1.5 in bromine.

The addition of bromine to cyclohexene in carbon tetrachloride initially attracted our attention as an example of a reaction having a negative overall energy of activation. There are a number of such reactions which are ionic processes occurring in non-polar environments, kinetically of high order and, being slow enough to be followed by conventional methods, necessarily with large negative overall entropies of activation. One early example was due to Davis,[2a] who studied the reaction of ethylene with $Br_2$ in the dark in dry $CCl_4$, and found that the rate increased progressively as the temperature was lowered from 25 to 0 °C. The addition of $Br_2$ to allyl acetate and chloroacetate showed similar behaviour.[3] More recently, other reactions exhibiting the same phenomenon have been described. Russian workers investigated the addition of halogens and nitrogen oxides to alkenes in non-polar solvents, or in the absence of a solvent, at low temperatures,[4-15] the bromination of oxiran olefins,[16] and the cleavage of ethers by alkyl-lithium compounds.[17-19] Coombes [20] found that nitration of some benzene homologues by anhydrous $HNO_3$ in $CCl_4$ showed a small increase in rate with a decrease in temperature, and Singh [21] referred briefly to a negative activation energy in the aminolysis of *p*-nitrophenyl trifluoroacetate in aprotic solvents.

The Russian workers proposed that the bromine-addition reactions proceed in stages, and that the enthalpy of reaction of the first stage exceeds the enthalpy of activation of the rate-determining stage. Since, however, the first stage does not proceed to near completion, it must have a strongly negative entropy of reaction: this implies that it is an aggregation process. Sergeev suggested [4,14] that a charge-transfer complex $C_6H_{10}{\cdot}Br_2$ is an intermediate in the bromination of cyclohexene (neat) and proposed that a second complex $C_6H_{10}{\cdot}2Br_2$ is formed before products are obtained. We show below that under certain conditions a reaction with a rate constant proportional to $[C_6H_{10}][Br_2]^2$ can be observed in carbon tetrachloride and that the reaction rate rises as the temperature falls. Either Sergeev's complex $C_6H_{10}{\cdot}Br_2$, or, in principle, the dimer $(Br_2)_2$, perhaps analogous to various interhalogen compounds $XY_3$, might be formed in a pre-equilibrium, reacting with the third molecule in the rate-determining step. As the temperature is lowered the fast pre-equilibrium will move towards complete formation of the intermediate $C_6H_{10}{\cdot}Br_2$ or $(Br_2)_2$, which will react in a second step with the third molecule in a reaction showing a normal positive temperature coefficient. This implies a maximum in the reaction rate: however, no reaction has yet been observed over a wide enough range of temperatures to show this behaviour.

A metastable charge-transfer complex between cyclohexene and bromine in carbon tetrachloride has indeed been reported [22] during the preparation of this manuscript, evidently with the requisite small formation constant although this was not measured. This raises a problem; the extinction coefficient of bromine, measured in carbon tetrachloride without additives, might be increased or decreased by the formation, to a small degree, of such a complex. Indeed, when small amounts of cyclohexene were added to such solutions, in the presence of *N*-bromosuccinimide (see below), the apparent extinction coefficient did increase, to an extent proportional to the amount of cyclohexene added. The slope of the linear plot of $\varepsilon_{app.}$ *versus* $[C_6H_{10}]$ was found to decrease with increasing temperature, as would be expected if the formation of the complex were exothermal, but its degree of formation was small because of an adverse entropy change. The effect was proved real by substituting cyclohexane for cyclohexene, when no perceptible increase in absorption intensity was observed. A plot of the slope of the $\varepsilon_{app.}/[C_6H_{10}]$ relationship against $1/T$ led to $\Delta H - 12.5$ kJ mol$^{-1}$ for complex formation, if one made the quite unjustifiable assumption that $\varepsilon$ for the complex was independent of temperature. This value does not quite allow us to rationalise the overall energetics of the addition reaction. However, values of $-22$ kJ mol$^{-1}$ ($-5.2$ kcal mol$^{-1}$) and 105 J K$^{-1}$ mol$^{-1}$ ($-25$ cal K$^{-1}$ mol$^{-1}$) for the enthalpy and entropy of formation for this complex would lead to *ca.* 2% and *ca.* 50% formation at 300 and 175 K, respectively, at an arbitrary concentration. $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values of 5 kJ mol$^{-1}$ (1.2 kcal mol$^{-1}$) and $-187$ J K$^{-1}$ mol$^{-1}$ ($-45$ cal K$^{-1}$ mol$^{-1}$) for the conversion of the complex plus bromine to the transition state leading to the bromonium ion tribromide, quite possibly an energetically undemanding but geometrically constrained process, would then rationalise our results (see below).

The possibility that $Br_2$ dimerises, reversibly and to a small extent, was checked by examining the absorption spectrum in carbon tetrachloride at 25° over a range of fairly high concentrations (0.01—0.1M). No evidence was obtained for this hypothesis, which accordingly received no further consideration.

Our initial investigation of the reaction between $C_6H_{10}$ and $Br_2$ in $CCl_4$ (with $[C_6H_{10}]$ *ca.* 5—150 × $10^{-3}$M, and $[Br_2]$ *ca.* 5 × $10^{-3}$M) gave measurable, but unreproducible, reaction rates. Purification of reactants and solvents by various methods

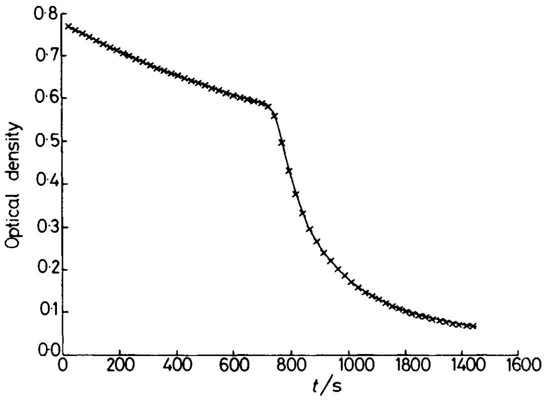


**Figure 1.** NBS-scavenged reaction, Phases 1 and 2. Digital trace, 60 points, 90% of reaction followed. Points experimental, line computer-drawn by connecting adjacent points

made little difference, except that fairly dry solvent had to be used if microheterogeneity of the reaction mixture, and very irregular reactions, were to be avoided; evidently the solubility of aqueous hydrobromic acid in $CCl_4$ is much lower than that of water. The effects of light, oxygen, and other radical traps (*e.g.* tri-t-butylphenol) were also examined, without improving the results, though bromine appeared to be disappearing in a roughly first-order process. Hydrogen bromide catalysed the reaction, and there was some evidence for autocatalysis of the slower reaction occurring between cyclohexene and bromine before the HBr was added. This autocatalysis was particularly marked when the $Br_2$–$CCl_4$ solution was shaken with solid sodium carbonate before the cyclohexene was added. These observations may be explained in terms of a reaction catalysed by HBr either as an impurity initially present, or formed as a product of a side-reaction. However, addition of bases such as pyridine, tri-n-propylamine, and diazabicyclo[2.2.2]octane to the reaction mixture proved unhelpful in improving reproducibility.

*N*-Bromosuccinimide (NBS) reacts rapidly and almost quantitatively with HBr to give succinimide and bromine,[23] and we hoped that this might provide a suitable way of removing HBr, however introduced, and hence allow a study of the principal reaction under consideration, of cyclohexene with bromine to give *trans*-1,2-dibromocyclohexane. One difficulty is that NBS is only slightly soluble in $CCl_4$; a saturated solution is *ca.* 2.5 × $10^{-3}$M at *ca.* 20 °C. The bromination reaction in the presence of NBS therefore occurred in two stages: a slow first phase, giving generally reproducible values for the third-order rate constant $k_3[C_6H_{10}][Br_2]^2$, followed by a sharp transition to a faster reaction, somewhat less reproducible (and of order 1.5 in bromine), once all the NBS had been consumed. Figure 1 (60 points, 90% of reaction followed) which is simply a plot of optical density at 416 nm against time mechanically logged and printed out, indicates this behaviour.

We emphasise that because of a tradition of poor agreement amongst different investigators of reactions of this type, and of the results of our own preliminary work, we have attempted to make as few prior assumptions as possible. Thus, kinetic orders were *not* first assumed, and then fitted to the data, and reaction products were *not* taken for granted. Optical densities at 416 nm, where only bromine absorbs, were logged mechanically, and the logarithm of the rate of change was plotted against that of the absolute value to give the kinetic order directly (van't Hoff's method [24]). Figure 2 (55 points, 62% of reaction followed) is the van't Hoff plot for both Phases 1 and 2 of the NBS-scavenged reaction, whilst Figure 3 (65 points, ρ 0.9938, 87% of reaction followed) is a van't Hoff plot for Phase 1 only. Results were usually, but not always, sufficiently precise to allow a mechanistic conclusion, and integral or half-integral. Appropriate rate constants were calculated and their logarithms plotted against those of the concentrations of other potentially relevant components, including water, to obtain experimental orders of reaction in these compounds. Most reactions were followed until the bromine concentration approached zero and became uncertain; many reaction products were analysed by g.l.c.

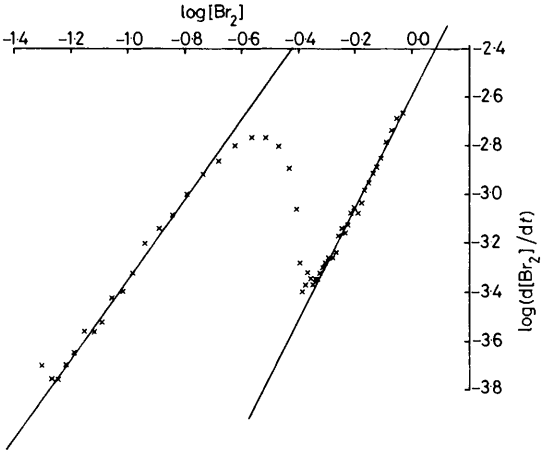


**Figure 2.** NBS-scavenged reaction, order plot of both Phases. 55 points, 62% of reaction followed. Points experimental, lines manually drawn. Phase 1, slope 2.2; Phase 2, slope 1.5

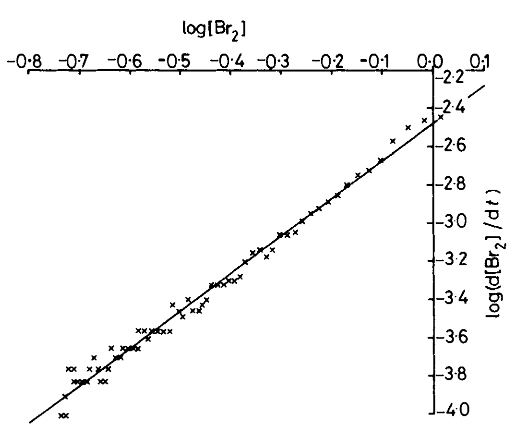


**Figure 3.** NBS-scavenged reaction, order plot of Phase 1 only, slope 1.96 ± 0.03, 65 points, ρ 0.993 78, 87% of reaction followed. Points experimental, line computer-drawn, linear least squares

This paper considers reactions in the presence of scavengers (*N*-bromoimides); the following paper describes experiments with added hydrogen bromide, with added succinimide or phthalimide, and those in the apparently simpler, but in reality more complex, system with no additive.

## Experimental

*Materials.*—Carbon tetrachloride (AnalaR) was dried over molecular sieves (type 5A, $\frac{1}{16}$ in pellets) where appropriate, and filtered. Cyclohexene was washed with aqueous acidic $FeSO_4$ solution, dried over anhydrous $Na_2SO_4$, distilled under nitrogen, and stored under nitrogen over molecular sieve (type 5A). Bromine (AnalaR) was used without further purification. Hydrogen bromide was obtained in 1 lb cylinders (B.D.H.). *N*-Bromosuccinimide (NBS) and *N*-bromophthalimide (NBP; Fluka) were recrystallised from glacial acetic acid, powdered, and dried *in vacuo*. Succinimide was recrystallised from water, dried in air, powdered, and dried *in vacuo*. *p*-Dibromobenzene was recrystallised from ethanol. *trans*-1,2-Dibromocyclohexane (Aldrich), 3-bromocyclohexene (Aldrich), bromocyclohexane, and bromobenzene were all purified by distillation. These four bromo-compounds, and cyclohexene itself, were all submitted to g.l.c. (see below) and found to be essentially pure. 3-Bromocyclohexene, however, underwent partial decomposition on the column, giving cyclohexadiene and HBr (see Discussion section). All these reagents had m.p.s or b.p.s corresponding to the literature values.

*trans*-2-Bromocyclohexanol was synthesised by the method of Hawkins and Bannard.[25] The bromohydrin crystallised from petroleum (b.p. 80—100 °C) at −30 °C and was collected, then recrystallised from the same solvent at 0 °C; m.p. 24 °C (*cf.* lit.,[25] 27 °C); it showed no impurities when submitted to g.l.c. (see below). 1-Bromocyclohexene was synthesised (in poor yield) by dehydrobrominating *trans*-1,2-dibromocyclohexane in boiling quinoline.[26] The product boiled at 76 °C and 25 mmHg (*cf.* lit.,[26] 58—60 °C and 15 mmHg), and g.l.c. (details below) showed it to contain small amounts of impurities. Its n.m.r. spectrum agreed with expectations. 2,4,4,6-Tetrabromocyclohexadienone was prepared according to the literature method,[27] m.p. 127—128 °C, (*cf.* lit.,[28] 124 °C).

*Analytical Procedures*.—Most spectrophotometric and kinetic studies were performed using a Cary 14 spectrophotometer. All reactions were followed by logging the absorption of light at 416 nm on tape (Datex punch) for subsequent data processing. The cell block was maintained at 20—45 (±0.1) °C using a Tamson water-bath. Cell-block temperatures below 20 °C were obtained using a Churchill thermo-regulator. The molar extinction coefficient for $Br_2$ in carbon tetrachloride was determined at 416 nm and found to be 210 l $mol^{-1}$ $cm^{-1}$ (*cf.* 208 at 417,[29] 205.9 l $mol^{-1}$ $cm^{-1}$ at 415 nm [30]). The molar extinction coefficient for water in $CCl_4$ was determined near 1.9 μm (first overtone of H–O stretching frequency) and found to be 1.9 l $mol^{-1}$ $cm^{-1}$. This figure was obtained using a formula which gives the solubility of water in $CCl_4$ at various temperatures.[31] Values for [$H_2O$] obtained throughout the whole of this investigation are the least reliable of the quantitative results quoted, because of the practical difficulties involved in determining them. Optical densities in the near i.r. of a solution of water in $CCl_4$ are small, and even when using a (0.0—0.1) slide-wire on the Cary 14 instrument, and 10 cm cells, the errors involved in determining the optical densities are large because of the relatively low signal : noise ratio. Other difficulties were caused by lack of a suitable reference sample, *i.e.* totally dry $CCl_4$: we used for this purpose a sample of $CCl_4$ which had been distilled from $P_2O_5$ and kept over molecular sieve. Saturated solutions of water in $CCl_4$ are not readily prepared by shaking water and $CCl_4$ together,[32] but when the lower layer resulting from such a procedure was filtered through a filter paper and then through a small amount of anhydrous $Na_2SO_4$, to remove water droplets, an homogeneous solution of water in $CCl_4$ remained. This was added to ' dry ' solvent, to give the desired concentration of water.

A specimen of cyclohexene, purified as described above, was examined spectroscopically in ethanol and found to contain no detectable amount of benzene, but it did show a maximum at *ca.* 260 nm, attributable to a trace of cyclohexa-1,3-diene (*ca.* 0.02%, assuming ε 10,000 [33]); a minor peak, probably this compound or cyclohexane, was also observed during g.l.c. (*ca.* 0.1%). Attempts to reduce these already low levels of impurities by distillation were not successful.

When solutions (0.011—0.095M) of bromine in carbon tetrachloride were examined in 1 mm cells, the relative optical densities at 382, 414, and 482 nm were found to be constant, within experimental error. There was therefore no evidence for the formation of a dimer, $Br_4$. When the absorbance near the maximum, at 412.7 nm, was measured as a function of temperature (measurements at 12, 25, and 33.4°) the temperature coefficient proved to be *ca.* −0.05% $degree^{-1}$.

Solutions of NBS in carbon tetrachloride showed only end-absorption from *ca.* 350 nm down to the cut-off at *ca.* 300 nm; the change in absorbance $\Delta E$ (using a 1 cm cell) at 415 nm was <0.001. Mixtures of NBS and cyclohexene had spectra with enhanced end-absorption at 300—350 nm, probably due to a weak charge-transfer complex, but no absorption at *ca.* 415 nm.

Solutions of bromine (4 $cm^3$), usually $(1.1 \pm 0.4) \times 10^{-3}$M, in carbon tetrachloride quarter-saturated with NBS, were treated with small amounts of cyclohexane or cyclohexene. The hydrocarbon (20—95 μl) was injected neat from a microsyringe, its volume being known to perhaps ±2 μl, the solvent being held in a 1 cm cuvette closed by a screw cap fitted with a Teflon-lined silicone rubber septum,[34] held in the thermostatted cell-compartment of a Unicam SP 1700 spectrophotometer. Immediately after mixing a chart-recorder was started, and intensity of absorption near the maximum for bromine (412.7 or 416 nm) was measured as a function of time. When cyclohexane was used, the expected negligible change occurred; when cyclohexene was employed, the absorption intensity was immediately increased, but then very slowly diminished as typical Phase 1 addition reactions occurred, extrapolation to time zero giving the desired increment in absorption intensity ($\Delta E$). After 5—9 such injections of varying amounts of hydrocarbon at each of four temperatures, plots of $\Delta E$ *versus* concentration were found to be linear (ρ 0.995—1.000), with slopes of 47.2 ± 1.2 (13°), 34.1 ± 0.3 (23.9°), 38.3 ± 0.8 (25.3°), and 29.9 ± 0.4 (40.1°) (the second measurement made at 416 rather than 412.7 nm). A similar experiment at 25.2° in the presence of $25 \times 10^{-4}$M-NBS (instead of $6.3 \times 10^{-4}$M) gave a slope of 41.6 ± 1.1. The blank experiment with cyclohexane replacing cyclohexene gave a meaningless slope of 1.0 ± 0.7, at 25.0°. A plot of these slopes against $1/T$ should give the enthalpy for complex formation, on the arbitrary (and implausible) assumption of constant extinction coefficient for the complex; this comes to $\Delta H - 12.5 \pm 0.3$ kJ $mol^{-1}$.

The shape of the absorbance *versus* wavelength curves was altered by the presence of cyclohexene, the broad maximum moving to shorter wavelengths, but we did not attempt to deduce the spectrum of the complex; even the slow Phase 1 addition reaction would make this difficult.

Solutions of NBS (and NBP) were prepared using a mechanical shaker. The concentration of bromoimide in any solution was found by adding solid KI and $H_2SO_4$ to a portion of the solution, and titrating the liberated $I_2$ with 0.01N-$Na_2S_2O_3$ solution. Again, because of the low solubility of NBS in $CCl_4$, the exact end-point could be difficult to detect but [NBS] could be determined more accurately than [$H_2O$].

A Perkin-Elmer F-11 gas chromatograph, fitted with a flame ionisation detector, was used. Analyses were performed on a 1 m column of $\frac{1}{8}$ in o.d. stainless steel packed with 25% May and Baker Embaphase silicone oil on F and M 60–80 mesh Diatoport S. The column temperature was 120 °C, and the carrier gas ($N_2$) inlet pressure 7.5 lb $in^{-2}$, giving a flow rate of *ca.* 22 ml $min^{-1}$. Under these conditions, the compounds listed below had the retention times (min) indicated: PhBr,

**Table 1.** NBS or NBP-scavenged reactions: Phase 1

| Run no. | $10^3[Br_2]$/ M | $10^3[C_6H_{10}]$/ M | $10^3[H_2O]$/ M | $10^3$[NBS]/ M | Temp. (°C) | %$Br_2$ used in Phase 1 | Order in $Br_2$ [a] | Pseudo-second-order rate constant [b] (l $mol^{-1}$ $s^{-1}$) | Third-order rate constant [c] ($l^2$ $mol^{-2}$ $s^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|
| 201 [d] | 3.34 | 78.9 | 2.1 | 1.6 | 25.1 | 50 [e] | 2.10 | 0.211 | 2.72 |
| 202 [d] | 3.34 | 98.7 | 2.1 | 1.6 | 25.1 | 56 [e] | 2.10 | 0.256 | 2.64 |
| 203 [d] | 3.34 | 118.4 | 2.1 | 1.6 | 25.1 | 60 [e] | 2.20 | 0.332 | 2.86 |
| 204 [d] | 3.34 | 138.1 | 2.1 | 1.6 | 25.1 | 64 [e] | 2.15 | 0.375 | 2.78 |
| 205 [d] | 3.34 | 157.8 | 2.1 | 1.6 | 25.1 | 59 [e] | 2.20 | 0.474 | 3.07 |
| 206 [d] | 3.34 | 177.6 | 2.1 | 1.6 | 25.1 | 58 [e] | 2.20 | 0.498 | 2.87 |
| 207 [f] | 3.34 | 78.9 | 2.1 | 1.6 | 35.2 | 48 [e] | 2.15 | 0.179 | 2.31 |
| 208 [f] | 3.34 | 78.9 | 2.1 | 1.6 | 44.6 | 35 [e] | 2.15 | 0.155 | 2.00 |
| 211 [f] | 3.34 | 78.9 | 2.1 | 1.6 | −3.0 | 67 | | 0.394 | 5.10 |
| 211A [f] | 3.34 | 78.9 | 2.1 | 1.6 | −3.0 | 64 | 2.1 | 0.387 | 5.01 |
| 213 [f] | 3.34 | 78.9 | 2.1 | 1.6 | 6.0 | 72 | 2.1 | 0.317 | 4.11 |
| 215 [f] | 3.34 | 78.9 | 2.1 | 1.6 | 14.5 | 66 | | 0.289 | 3.74 |
| 217 [g] | 2.89 | 59.2 | 1.3 | 0.225 | 25.4 | 22 | | 0.130 | 2.22 |
| 218 [g] | 2.89 | 59.2 | 1.4 | 0.45 | 25.4 | 43 | | 0.131 | 2.25 |
| 219 [g] | 2.89 | 59.2 | 1.4 | 0.36 | 25.4 | 36 | | 0.135 | 2.31 |
| 220 [g] | 2.89 | 59.2 | 1.3 | 0.135 | 25.4 | 9 | | 0.138 | 2.36 |
| 221 [g] | 2.89 | 59.2 | 1.3 | 0.09 | 25.4 | 5 | | 0.130 | 2.22 |
| 279 [h] | 4.04 | 78.9 | 2.3 | 2.0 + 0.2 [i] | 25.4 | 59 [e] | 2.30 | 0.221 | 2.87 |
| 280 [h] | 4.04 | 78.9 | 2.3 | 2.0 + 0.3 [i] | 25.4 | 60 [e] | 1.95 | 0.264 | 3.42 |
| 281 [h] | 4.04 | 78.9 | 2.3 | 2.0 + 0.5 [i] | 25.4 | 71 [e] | 2.05 | 0.240 | 3.12 |
| 282 [h] | 4.04 | 78.9 | 2.3 | 2.0 + 0.6 [i] | 25.4 | 62 [e] | 2.25 | 0.225 | 2.92 |
| 283 [h] | 4.04 | 78.9 | 2.3 | 2.0 + 0.8 [i] | 25.4 | 66 | 2.10 | 0.227 | 2.94 |
| 284 [h] | 4.04 | 78.9 | 2.3 | 2.0 + 0.9 [i] | 25.4 | 51 | 2.20 | 0.229 | 2.97 |
| 285 [h] | 4.04 | 78.9 | 2.3 | 2.0 + 1.5 [i] | 25.4 | 42 | 2.15 | 0.227 | 2.93 |
| 260 [j] | 3.72 | 59.2 | 1.0 | 0.32 | 25.4 | 26 | 2.20 | 0.128 | 2.20 |
| 261 [j] | 3.72 | 59.2 | 1.1 | 0.32 | 25.4 | 26 | 1.8 | 0.141 | 2.43 |
| 262 [j] | 3.72 | 59.2 | 1.3 | 0.32 | 25.4 | 24 | | 0.131 | 2.25 |
| 263 [j] | 3.72 | 59.2 | 1.7 | 0.32 | 25.4 | 22 | 2.3 | 0.127 | 2.17 |
| 264 [j] | 3.72 | 59.2 | 2.2 | 0.32 | 25.4 | 24 | | 0.140 | 2.39 |
| 265 [j] | 3.72 | 59.2 | 2.6 | 0.32 | 25.4 | 23 | | 0.155 | 2.65 |
| 266 [j] | 3.72 | 59.2 | 3.1 | 0.32 | 25.4 | 18 | | 0.150 | 2.56 |
| 223 [k] | 6.72 | 118.4 | 1.7 | 1.85 | 25.1 | 72 | 2.2 | 0.409 | 3.57 |
| 224 [k] | 5.37 | 118.4 | 1.7 | 1.85 | 25.1 | 78 | 2.1 | 0.355 | 3.09 |
| 225 [k] | 4.03 | 118.4 | 1.7 | 1.85 | 25.1 | 68 [e] | 2.15 | 0.305 | 2.64 |
| 226 [k] | 2.69 | 118.4 | 1.7 | 1.85 | 25.1 | 51 [e] | 2.45 | 0.258 | 2.22 |
| 227 [k] | 1.34 | 118.4 | 1.7 | 1.85 | 25.1 | 39 [e] | | 0.229 | 1.97 |
| 229 [k] | 12.34 | 197.3 | 1.9 | 2.0 | 25.4 | 65 | 3.3 | 1.645 | 8.68 |
| 230 [k] | 9.87 | 197.3 | 1.9 | 2.0 | 25.4 | 67 | 2.9 | 1.107 | 5.82 |
| 231 [k] | 7.40 | 197.3 | 1.9 | 2.0 | 25.4 | 94 [e] | 1.9 | 0.908 | 4.78 |
| 232 [k] | 4.93 | 197.3 | 1.9 | 2.0 | 25.4 | 87 [e] | 1.95 | 0.623 | 3.26 |
| 233 [k] | 2.47 | 197.3 | 1.9 | 2.0 | 25.4 | 61 [e] | 1.95 | 0.556 | 2.89 |
| 234 [k] | 1.23 | 197.3 | 1.9 | 2.0 | 25.4 | 57 [e] | | 0.474 | 2.46 |
| 475 [l] | 4.39 | 78.9 | 0.3 | 0.70 [l] | 25.3 | 83 [e] | 1.70 | 0.229 | 2.99 |
| 476 [l] | 4.39 | 78.9 | 0.3 | 0.28 [l] | 25.3 | 33 | 2.5 | 0.180 | 2.32 |
| 479 [l] | 4.39 | 78.9 | 0.3 | 0.21 [l] | 25.3 | 19 | | 0.189 | 2.43 |
| 480 [l] | 4.39 | 78.9 | 0.3 | 0.35 [l] | 25.3 | 35 | 1.8 | 0.185 | 2.39 |
| 481 [l] | 4.39 | 78.9 | 0.3 | 0.42 [l] | 25.3 | 47 | 1.75 | 0.199 | 2.57 |

[a] The order in $Br_2$ is not shown for a few rapid reactions which gave too few points to permit a reasonably good order plot to be obtained. Values are quoted to the nearest 0.05 when at least 30 data points were used, otherwise to the nearest 0.1. Standard errors in the values of the order in $Br_2$ lie in the range 1—10% for the runs quoted in this Table. [b] Rate expression: $-d[Br_2]/dt = k_2'[Br_2]^2$. Standard errors in the slopes of the second-order plots (from which the pseudo-second-order rate constants were calculated) lie in the range 0.2—0.9% for the runs quoted in this Table. [c] $k_3 = k_2'/[C_6H_{10}]$. [d] Runs 201—206. Order in $C_6H_{10}$: 1.12 ± 0.06. [e] Phase 1 not followed to completion; value quoted is extent of reaction followed. [f] Runs 207—215. Third-order rate constants are corrected for thermal expansion of solvent and cell. [g] Runs 217—221. Order in NBS: 0.00 ± 0.02. Consumption of NBS: 0.32 ± 0.02 mole per mole $Br_2$. [h] Runs 279—285. Order in succinimide: −0.03 ± 0.04. [i] [NBS] + [S], where S = succinimide. [j] Runs 260—266. Order in $H_2O$: 0.13 ± 0.05. [k] Runs 223—227 and 229—234 prove involvement of reaction of order in $Br_2$ higher than 2; where order plots give slopes diverging much from 2, the second-order plots are, of course, not truly linear, but the sensitivity of the computed third-order rate constant to $[Br_2]$ confirms the significance of reactions of order in bromine higher than 2. [l] Runs 475—481. NBP used in place of NBS. Order in NBP: 0.18 ± 0.06. Consumption of NBP: 0.17 ± 0.02 mole per mole $Br_2$.

2.3; 1-bromocyclohexene, 3.1; 3-bromocyclohexene, 3.4; *trans*-2-bromocyclohexanol, 5.9; *p*-dibromobenzene, 9.0; *trans*-1,2-dibromocyclohexane, 11.4. Bromocyclohexane had the same retention time as 1-bromocyclohexene, and as these compounds were not resolved from one another, no attempt was made to determine them quantitatively, but 3-bromocyclohexene was sufficiently resolved from these compounds for quantitative analyses to be made. The internal standard method[35] was used for quantitative analysis, with PhBr serving as internal standard for 3-bromocyclohexene, and *p*-

**Table 2.** NBS or NBP-scavenged reactions: Phase 2

| Run no. | $10^3[Br_2]$/ M | $10^3[C_6H_{10}]$/ M | $10^3[H_2O]$/ M | $10^3$[NBS]/ M or $10^3$[NBP]/ M | Temp. (°C) | % $Br_2$ consumed in Phase 2 | Order in $Br_2$ [a] | Pseudo-1.5-order rate constant ($l^{0.5}$ $mol^{-0.5}$ $s^{-1}$) [b] | 2.5-order rate constant ($l^{1.5}$ $mol^{-1.5}$ $s^{-1}$) [c] | Third-order rate constant ($l^e$ $mol^{-2}$ $s^{-1}$) [d] |
|---|---|---|---|---|---|---|---|---|---|---|
| 269 [e] | 3.72 | 19.7 | 0.8 | 0.12 | 25.4 | 39 | 1.50 | 0.0142 [c] | 0.76 | 69 |
| 270 [e] | 3.72 | 39.5 | 0.8 | 0.12 | 25.4 | 48 | 1.30 | 0.0237 [c] | 0.65 | 59 |
| 271 [e] | 3.72 | 59.2 | 0.8 | 0.12 | 25.4 | 72 | 1.35 | 0.0332 [c] | 0.59 | 54 |
| 272 [e] | 3.72 | 78.9 | 0.8 | 0.12 | 25.4 | 67 | 1.40 | 0.0445 [c] | 0.59 | 54 |
| 273 [e] | 3.72 | 98.7 | 0.8 | 0.12 | 25.4 | 71 | 1.35 | 0.0603 [c] | 0.63 | 58 |
| 274 [e] | 3.72 | 118.4 | 0.8 | 0.12 | 25.4 | 72 | 1.50 | 0.0618 [c] | 0.54 | 49 |
| 275 [e] | 3.72 | 138.1 | 0.8 | 0.12 | 25.4 | 73 | 1.50 | 0.0676 [c] | 0.50 | 46 |
| 276 [e] | 3.72 | 157.8 | 0.8 | 0.12 | 25.4 | 72 | 1.50 | 0.0786 [c] | 0.51 | 47 |
| 277 [e] | 3.72 | 177.6 | 0.8 | 0.12 | 25.4 | 76 | 1.45 | 0.0922 [c] | 0.54 | 49 |
| 278 [e] | 3.72 | 197.3 | 0.8 | 0.12 | 25.4 | 82 | 1.50 | 0.0948 [c] | 0.50 | 46 |
| 217 [f] | 2.89 | 59.2 | 1.3 | 0.225 | 25.4 | 62 | 1.5 | 0.0770 [d] | 1.35 | 90 |
| 218 [f] | 2.89 | 59.2 | 1.4 | 0.45 | 25.4 | 48 | 1.5 | 0.145 [d] | 2.57 | 121 |
| 219 [f] | 2.89 | 59.2 | 1.4 | 0.36 | 25.4 | 50 | 1.6 | 0.123 [d] | 2.17 | 114 |
| 220 [f] | 2.89 | 59.2 | 1.3 | 0.135 | 25.4 | 72 | 1.4 | 0.0442 [d] | 0.78 | 67 |
| 221 [f] | 2.89 | 59.2 | 1.3 | 0.09 | 25.4 | 71 |  | 0.0348 [d] | 0.61 | 64 |
| 222 [f] | 2.89 | 59.2 | 1.3 | 0.045 | 25.4 | 70 |  | 0.0313 [d] | 0.55 | 82 |
| 260 [g] | 3.72 | 59.2 | 1.0 | 0.32 | 25.4 | 55 | 1.65 | 0.1049 [e] | 1.87 | 105 |
| 261 [g] | 3.72 | 59.2 | 1.1 | 0.32 | 25.4 | 56 | 1.75 | 0.1052 [e] | 1.88 | 105 |
| 262 [g] | 3.72 | 59.2 | 1.3 | 0.32 | 25.4 | 57 | 1.7 | 0.0980 [e] | 1.75 | 98 |
| 263 [g] | 3.72 | 59.2 | 1.7 | 0.32 | 25.4 | 60 | 1.75 | 0.0951 [e] | 1.69 | 94 |
| 264 [g] | 3.72 | 59.2 | 2.2 | 0.32 | 25.4 | 59 | 1.7 | 0.0984 [e] | 1.75 | 98 |
| 265 [g] | 3.72 | 59.2 | 2.6 | 0.32 | 25.4 | 62 | 1.7 | 0.0924 [e] | 1.64 | 92 |
| 266 [g] | 3.72 | 59.2 | 3.1 | 0.32 | 25.4 | 60 | 1.8 | 0.0933 [e] | 1.66 | 93 |
| 267 [g] | 3.72 | 59.2 | 3.5 | 0.32 | 25.4 | 58 | 1.60 | 0.0974 [e] | 1.73 | 97 |
| 476 [h] | 4.39 | 78.9 | 0.3 | 0.28 | 25.3 | 50 | 1.6 | 0.1111 | 1.48 | *i* |
| 477 [h] | 4.39 | 78.9 | 0.3 | 0.07 | 25.3 | 69 | 1.50 | 0.0269 | 0.357 | *i* |
| 478 [h] | 4.39 | 78.9 | 0.3 | 0.14 | 25.3 | 62 | 1.55 | 0.0424 | 0.564 | *i* |
| 479 [h] | 4.39 | 78.9 | 0.3 | 0.21 | 25.3 | 63 | 1.50 | 0.0761 | 1.011 | *i* |
| 480 [h] | 4.39 | 78.9 | 0.3 | 0.35 | 25.3 | 41 | 1.5 | 0.1501 | 2.01 | *i* |
| 481 [h] | 4.39 | 78.9 | 0.3 | 0.42 | 25.3 | 41 | 1.5 | 0.1940 | 2.59 | *i* |
| 482 [h] | 4.39 | 78.9 | 0.3 | 0.04 | 25.3 | 75 | 1.45 | 0.0219 | 0.290 | *i* |
| 483 [h] | 4.39 | 78.9 | 0.3 | 0.03 | 25.3 | 70 | 1.55 | 0.0178 | 0.236 | *i* |
| 484 [h] | 4.39 | 78.9 | 0.3 | 0.01 | 25.3 | 68 | 1.55 | 0.0166 | 0.220 | *i* |
| 485 [h] | 4.39 | 78.9 | 0.3 | 0 | 25.3 | 65 | 1.55 | 0.0163 | 0.217 | *i* |

[a] Values are quoted to the nearest 0.05 when at least 30 data points were used, otherwise to the nearest 0.1. Standard errors in the values of the order in $Br_2$ lie in the range 1.4—6.1% for the runs quoted in this Table. [b] Rate expression: $-d[Br_2]/dt = k'_{1.5}[Br_2]^{1.5}$. Standard errors in the slopes of the 1.5-order plots (from which the pseudo-1.5-order rate constants were calculated) lie in the range 0.1—2.7% for the runs quoted in this Table. [c] $k_{2.5} = k'_{1.5}/[C_6H_{10}]$. [d] $k_3 = k'_{1.5}/[C_6H_{10}][S]^{0.5}$, where [S] = concentration of 'consumed NBS.' [e] Runs 269—278. Order in $C_6H_{10}$: 0.83 ± 0.02. 2.5-order rate constant: 0.47 ± 0.02 $l^{1.5}$ $mol^{-1.5}$ $s^{-1}$. [The first value was obtained by plotting log (pseudo-1.5-order rate constant) *vs.* log $[C_6H_{10}]$. The line did not pass exactly through the origin, which accounts for the discrepancy between this value and those listed.] Another block of seven runs with $[Br_2]$ 4.18 × $10^{-3}$M gave similar results, with third-order rate constants in the range 41—64 $l^2$ $mol^{-2}$ $s^{-1}$. [f] Runs 217—222. Order in 'consumed NBS': 0.73 ± 0.10. [g] Runs 260—267. Order in $H_2O$: −0.08 ± 0.03. [h] Runs 476—485. NBP used in place of NBS. Order in 'consumed NBP': 1.70 ± 0.07. [This value was obtained by plotting log [NBP] *vs.* log $(k_{2.5} - {}_0k_{2.5})$, where $k_{2.5}$ is the 2.5-order rate constant for runs 476—484 and ${}_0k_{2.5}$ is the 2.5-order rate constant for run 485 in which no NBP was added.] Another block of similar runs gave an order in 'consumed NBP' of 1.33 ± 0.11, the only material difference being that $[Br_2]$ = 5.94 × $10^{-3}$M. [i] No third-order rate constant is quoted for the NBP-scavenged reactions. It is obvious (note *h*) that the order in 'consumed NBP' is far greater than 0.5, and third-order rate constants based on the assumption of a term $[NBP]^{0.5}$ are unjustified.

dibromobenzene for *trans*-2-bromocyclohexanol and *trans*-1,2-dibromocyclohexane. Peak-height ratios were used.[35]

*Kinetic Measurements.*—Solutions of $Br_2$ of known (weight in volume) concentration were prepared in $CCl_4$ containing NBS, as required. Reactions were carried out in 1 cm screw top capped spectrophotometer cells.[34] When the cell had reached thermostat temperature in the cell-holder, a calculated amount of cyclohexene was injected through the septum into the cell, using a Hamilton 50 µl or 100 µl syringe. The cell was shaken briefly and returned to the cell-holder. Some mixtures of reaction products were analysed by g.l.c., after internal standards had been added.

Reaction orders and rate constants were calculated by computer, initially an Elliott-503, subsequently an ICL 4-75, fitted with a Calcomp plotter. The programs used allowed us to obtain graphs from our data, showing the latter plotted for various assumed reaction orders, and also provided an experimental value *n* of the reaction order, using van't Hoff's method[24] (rate = $kc^n$, ∴ log rate = $n$ log c + log $k$). Instantaneous values for reaction rates were calculated as follows. Optical densities $A(1)$, $A(2) \cdots A(N)$ were recorded at a time interval ($t_{int}$) apart. The rate at any time was then calculated from Rate $(i) = \{A(i+1) - A(i-1)\}/2t_{int}$. Thus the rate is an approximate value of the tangent to the curve, midway between two optical densities on the optical density–time curve. Such plots of log (instantaneous rate) against log (optical density) are subsequently described as 'order plots'.

There are several reaction parameters which can be altered, *e.g.* temperature, and the concentrations of cyclohexene, NBS, and $H_2O$. The effect of added succinimide, to which the NBS is mainly converted, was also investigated. Several blocks of runs were performed, in each of which one of these parameters was varied.

Succinimide was not the only product formed from NBS during Phase 1. Some insoluble, probably polymeric, material deposited on the cell walls, and could only be removed mechanically; early runs, possibly affected by this problem, are not included in Table 1.

## Results

The reactions described in this paper are referred to as ' NBS-scavenged ' and considered to be carried out in the initial absence of HBr, otherwise normally present. Other types of reaction will be discussed in Part 2.

Rate constants quoted in Tables 1 and 2 were corrected by taking into account the changes in concentrations of reactants caused by addition of cyclohexene to the cell at the start of each reaction, the change in $[C_6H_{10}]$ during the course of a reaction (*i.e.* by using the cyclohexene concentration present halfway through the phase of the reaction for which data are listed), and the change in $\varepsilon$ for bromine produced by reversible complex formation, at the temperature and cyclohexene content for that run. All concentrations quoted in Tables 1 and 2 are the actual initial values for each run before the above corrections were applied.

## Discussion

In all our work, cyclohexene was initially present in large excess. As Figure 1 shows, reactions between $Br_2$ and cyclohexene in the presence of *N*-bromosuccinimide take place in two stages: a slow phase, in which the bromoimide is present in excess, and a fast phase after it has been consumed by reactions producing HBr. In the first phase (a) order plots [see Figures 2 and 3; see also Figure 4 (25 points, $\rho$ 0.999 96, 22% of reaction followed) which is a second-order plot of the disappearance of bromine] indicate a reaction order in bromine of 2, or more at higher initial $Br_2$ concentrations, when, however, data become less accurate; (b) calculated second-order rates for disappearance of $Br_2$ are precise and proportional to $[C_6H_{10}]$; and (c) third-order rate constants, $k_3[Br_2]^2[C_6H_{10}]$, do not vary when concentrations of NBS vary, or when succinimide is added to the reaction mixture. The slight variation in $k_3$ with water content, if real, is presumably a general solvent effect.

Experimental results supporting these generalisations are given in Table 1. Other workers [30,36,37] have found the same rate law (*i.e.* rate = $k_3$ [alkene]$[Br_2]^2$) in the reaction between bromine and acyclic alkenes in solvents of relatively low polarity. However, the addition of $Br_2$ to *trans*-stilbene showed a rate constant of $0.032 \pm 0.006$ $l^2$ $mol^{-2}$ $s^{-1}$ (at 25 °C) in $CCl_4$, but a value of $58.4 \pm 2.4$ $l^2$ $mol^{-2}$ $s^{-1}$ (at 25 °C) in $(CH_2Cl)_2$ [dielectric constants of $CCl_4$ and $(CH_2Cl)_2$ are 2.2 and 10.2 respectively [36]]. A very recent investigation [38] using the stopped-flow technique of the reaction between $Br_2$ and cyclohexene in the presence of pyridine in $(CH_2Cl)_2$ showed that in this solvent, if the pyridine were omitted, $k_3$ was $(2.39 \pm 0.16) \times 10^5$ $l^2$ $mol^{-2}$ $s^{-1}$, *ca.* $10^5$ times larger than our rate constants in $CCl_4$. It is obviously not easy to compare our reactions in $CCl_4$ with those, performed in more polar media, which are very much faster, and the similarity in kinetic form might not correspond to similarity in mechanism.

It seems legitimate to regard the rate-determining step of this reaction as leading to the tribromide (pentabromide, *etc.*) of the bromonium ion. There is no evidence that a significant term exists in $[Br_2]$ giving the bromonium monobromide. This explains the success of the Ziegler allylic bromination of cyclohexene in carbon tetrachloride, given the now established mechanism for this reaction; [39] a very low concentration of $Br_2$ will react with cyclohexene immeasurably slowly by the route discussed here, so that an opportunity exists for a radical-chain process, first order in $Br_2$, leading to a very different product composition. We cannot, of course, exclude the possibility that at $[Br_2] \ll 10^{-3}$M the first-order ionic process might become significant; however the second-order term, first order in bromine, recently reported [22] for the bromine–cyclohexene reaction carried out in carbon tetrachloride in the absence of a scavenger is much faster than the rates we have observed, and we must ascribe it to a catalysed process (see Part 2). Anyone who wishes to accept the reported [22] second-order rate constant of 0.011 l $mol^{-1}$ $s^{-1}$ (incompatible with our experimental results) as representing a simple reaction proportional to $[Br_2][C_6H_{10}]$ will have to explain (a) the success of Ziegler bromination; (b) why the addition reaction is inhibited by NBS and NBP (see below), and (c) why catalysis of the addition reaction by succinimide and phthalimide (following paper) ceases in the presence of even small amounts of *N*-bromoimides.

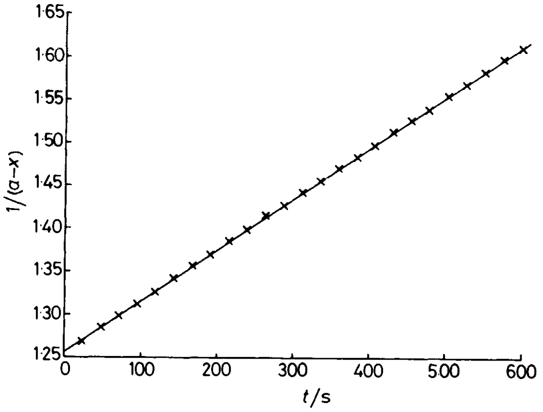


**Figure 4.** NBS-scavenged reaction, Phase 1. Second-order plot of disappearance of bromine. 25 points, $\rho$ 0.999 96, 22% of reaction followed. Points experimental, line computer-drawn

The effect of temperature was investigated in the range −3 to +44.6 °C, leading to values of $\Delta H^\ddagger$ at 20 °C of $-16.6 \pm 0.6$ kJ $mol^{-1}$ ($-4.0 \pm 0.1$ kcal $mol^{-1}$) and $\Delta S^\ddagger$ $-292 \pm 3$ J $K^{-1}$ $mol^{-1}$ ($-70 \pm 1$ cal $K^{-1}$ $mol^{-1}$).

*N*-Bromophthalimide reacts very rapidly with HBr, and should be able to replace NBS. Not only did we find this to be so, but the third-order rate constant for Phase 1 of the reaction was identical (within experimental error) with that found when NBS was used. This is additional evidence for the proposal that NBS merely acts as a scavenger of HBr in phase 1 of the reaction, and that any otherwise inert compound that can react in this way will be satisfactory, providing that its reaction with HBr is fast enough. Interestingly, 2,4,4,6-tetrabromocyclohexadienone is unsatisfactory in this context, because its reaction with HBr is measurably slow.

In Phase 2 of the reaction in the presence of NBS or NBP (a) order plots indicate a reaction of order 1.5, or rather higher, in $Br_2$ [see Figure 5 (70 points, $\rho$ 0.999 94, 75% of reaction followed) which is a 1.5-order plot of the disappearance of bromine in Phase 2 of an NBP-scavenged reaction] and (b) calculated 1.5-order rates for disappearance of $Br_2$ are fairly precise and proportional to $[C_6H_{10}]$ (used in large excess).

We found that the 2.5-order rate constant for Phase 2 *was* affected by [' consumed NBS '] (experimental order in this

**Table 3.** NBS-inhibited reactions: product analyses

| Run no. | Reaction | % Br atom recovery [a] | mole % 1,2-$Br_2$Cy [b] | mole % 3-BrCy [c] | mole % 2-BrOHCy [d] |
|---|---|---|---|---|---|
| | $Br_2$, $C_6H_{10}$, no NBS, dark | | 92.9 | 4.8 | |
| | $Br_2$, $C_6H_{10}$, no NBS, sunlight | | 66.8 | 18.1 | |
| | Blank ($C_6H_{10}$, NBS, no $Br_2$) | | | 0 | |
| 217—222 | [NBS] varying | 86—99 | 83—97 | 1—2 | 0.7—2.0 |
| 201—206 | [$C_6H_{10}$] varying | 72—81 (mainly 78—81) | 69—79 (mainly 74—79) | 1.5—2.7 | 0.8—2.1 |
| 207—215 | temperature varying | 79—87 | 75—87 | 0.5—4.4 | 0.7—3.1 |
| 223—227, 229—234 | [$Br_2$] varying, [NBS] constant | 57—95 | main product | small amounts | |

[a] See Discussion section. [b] *trans*-1,2-Dibromocyclohexane. [c] 3-Bromocyclohexene. [d] *trans*-2-Bromocyclohexanol.
*N.b.* bromocyclohexane and 1-bromocyclohexene (inseparable) were not detected.

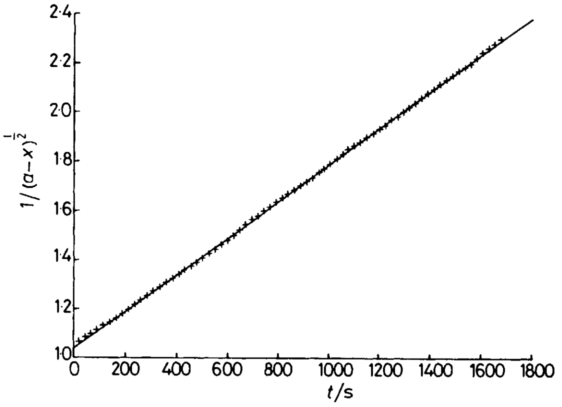
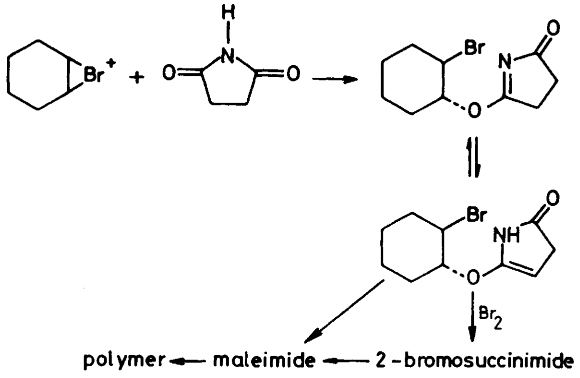


**Figure 5.** NBP-scavenged reaction, Phase 2. 1.5-Order plot of disappearance of bromine. 70 points, ρ 0.999 94, 75% of reaction followed. Points experimental, line computer-drawn



component 0.73 ± 0.10). We also found that [$H_2O$] had no measurable effect on the order in $Br_2$ or rate constant of the second phase of the NBS-scavenged reaction. Although NBP showed largely similar behaviour to NBS, the order in ' consumed NBP ' was high (1.70 ± 0.07 and 1.33 ± 0.11 in two blocks of runs) and reactions in Phase 2 when initial [NBP] was high were rapid. Plainly, some explanation is called for. Further discussion of Phase 2 is deferred to the following paper.

In the NBS-scavenged reactions, the Phase 1 reaction which is second order in $Br_2$ will presumably continue to contribute to the second (faster) phase of the reaction of bromine with cyclohexene. The contribution is always small: in a number of cases, the reaction proportional to $[Br_2]^2$ constituted 1.6—7.1% of the overall reaction (*i.e.* disappearance of bromine), reaching 13.5% only in the case of a reaction showing a very long first phase and short second phase. The NBP-scavenged reactions showed similar behaviour, a contribution of 4% being calculated in the example studied.

*Product Analysis.*—Some typical results are shown in Table 3. *trans*-1,2-Dibromocyclohexane was invariably the main product. 1-Bromocyclohexene and bromocyclohexane were not detected, but trace amounts of other products could be seen in chromatograms of the reaction products. 3-Bromocyclohexene underwent some decomposition on the column even when the most inert solid support available was used. The bromohydrin was presumably formed from the small quantities of water present.

Lower bromine-atom recoveries were observed when smaller amounts of NBS were present, in a block of runs in which [NBS] varied, but the variation in the recovery was random within the small number of runs. In a series of reactions in which [$Br_2$] varied whilst [NBS] was constant, the bromine-atom recovery reached 95% at high values of [$Br_2$] falling to 57% when [NBS] = 3[$Br_2$] at the start of the reaction. In some of these reactions the NBS was not entirely consumed (*i.e.* reaction entirely Phase 1), so that not all the initial Br could be recovered as products. One problem which remains unresolved is that the consumption of NBS in Phase 1 of the reaction is 0.32 ± 0.02 mole per mole $Br_2$ (see footnote *g* to Table 1) whilst the identified reaction products whose formation is accompanied by liberation of equimolar amounts of HBr (3-bromocyclohexene and *trans*-2-bromocyclohexanol) are not found in quantities which could give rise to this consumption of NBS (see Table 3). Similarly, the consumption of NBP is 0.17 ± 0.02 mole per mole of $Br_2$. One possible explanation is the formation of larger amounts of 3-bromocyclohexene than recorded in Table 3, followed by reaction of this with $Br_2$, more rapid than the reaction of the excess of cyclohexene present, to give 1,2,3-tribromocyclohexane which would not have been detected by g.l.c. under the operating conditions used. Alternatively, the allylic bromide might undergo catalysed elimination of hydrogen bromide, giving ultimately either a tetrabromocyclohexane or perhaps benzene or bromobenzene. (In the absence of excess of bromine, *etc.*, 3-bromocyclohexene is stable at the reaction temperature.) More probable explanations involve the NBS and succinimide components as such. Enolisation would obviously allow electrophilic attack by bromine or loss of a proton to give maleimide. Nucleophilic participation in the opening of the bromonium cation would also probably lead to *C*-brominated products; and perhaps maleimide or polymaleimide (see above).

To summarise, our hypothesis is that in carbon tetrachloride in the presence of *N*-bromoimide scavengers, bromine reacts with cyclohexene to give the tribromide (pentabromide, *etc.*) of the bromonium cation, in the rate-determining step of a rather slow reaction, proportional in its duration to the concentration of scavenger, but independent of the nature and amount of scavenger in reaction order and rate. Addition of water should and does diminish the length of this slow phase; addition of the corresponding imide has no effect. Allylic bromination under Ziegler conditions involves a radical-chain mechanism unrelated to the ionic processes studied here; illumination promotes this and gives the expected shift in the substitution : addition ratio. A second, and more rapid, ionic reaction occurs when no scavenger is present or when the scavenger initially present has been consumed. This is of order 1.5 in bromine, and is discussed further in the following paper.

Reactions which, like the slow '$Br_4$' reaction described here, have a negative overall activation enthalpy may be synthetically advantageous and deserve mechanistic study. Interest in this area is reviving.[40]

## Acknowledgements

We thank Dr. P. A. Bristow for advice and assistance with computer programs.

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*Received* 27*th August* 1982; *Paper* 2/1491