The Reaction of Bromine with Cyclohexene in Carbon Tetrachloride. Part 2.[1] Reactions in the Presence of Added Hydrogen Bromide, and of Imides, and in the Absence of Additives[2]

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The addition of bromine to cyclohexene in carbon tetrachloride containing added hydrogen bromide takes place rapidly, and is of first order in each of these species. When bromine is added to cyclohexene in solutions containing succinimide or phthalimide, the addition reaction follows an expression of order 1.5 in bromine and 0.5 in the imide. When no other component is present, the addition of bromine to cyclohexene is extremely sensitive to unintentional additives, but is usually of order 1.5 in bromine and of small positive order in water. We suggest reasonable reaction mechanisms for these processes, involving species stoicheiometrically equivalent to HBr_3 and HBr_5, and discuss their applicability to the second, fast phase of the scavenged reactions described in Part 1.

In Part 1 we described the reaction between bromine and cyclohexene in carbon tetrachloride in the presence of scavengers for hydrogen bromide, *viz.* *N*-bromosuccinimide (NBS) and *N*-bromophthalimide (NBP). This occurs in two phases. In the first, scavenger is still present, and the reaction rate (disappearance of bromine, measured spectrophotometrically) is proportional to $[\text{cyclohexene}][Br_2]^2$ (with terms corresponding to higher orders in bromine becoming important at higher concentrations). This can be described as ' the Br_4 reaction ', meaning the reaction with a transition state of stoicheiometry cyclohexene·Br_4, and rationalised as involving the formation of the tribromide of the bromonium cation. In the second phase, after the scavenger has been consumed, the rate is proportional to $[\text{cyclohexene}][Br_2]^{1.5}$. This process was initially rationalised (see Scheme 1) as involving catalysis of the addition reaction by the small amount of HBr presumably in equilibrium with succinimide or phthalimide, formed from scavenger, plus excess of bromine, which would lead to the hydrodibromide of the bromonium cation and may be called ' the HBr_3 reaction '. We therefore describe experiments which verify catalysis by HBr, estimate its efficiency and, in the event, necessitate a different explanation. We then discuss the reactions observed in the absence of any intentional additive, which are the most difficult to understand.

Experimental

Materials.—Bromine, cyclohexene, CCl_4, HBr, and succinimide, were all commercially available products, obtained and purified as described previously.[1] Phthalimide (commercially available) was recrystallised from ethanol, powdered, and dried *in vacuo*. Saturated solutions of succinimide and phthalimide in CCl_4 were prepared at 25 °C using a mechanical shaker (as with NBS[1]). The concentration of a batch of solution so prepared was determined by evaporating a known volume of solution to dryness, and found to be 1.56×10^{-3}M for succinimide and 1.63×10^{-3}M for phthalimide.

Kinetic Measurements.—The methods used have already been described. For the investigation of the effect of varying [HBr], solutions of Br_2 in CCl_4 and HBr in CCl_4 were prepared. A known volume of the HBr solution was transferred to a 50 ml graduated flask, the contents of which were then made up to the mark with CCl_4 and mixed thoroughly, and a 5 ml portion of this solution was then pipetted into an excess of NBS-saturated CCl_4 and the liberated bromine estimated spectrophotometrically; this established the concentration of the HBr solution. To the remaining (45 ml) HBr solution, a Br_2–CCl_4 solution (3 ml) was added, the solution was shaken well, and a 5 ml sample was transferred to the spectrophotometer cell.[1] An excess of cyclohexene was injected and the reaction followed as described in Part 1.[1] Detailed product analyses (see Part 1[1]) were not performed, but g.l.c. of the products showed that in all the types of reactions described in this paper the main product was again *trans*-1,2-dibromocyclohexane, with small amounts of 3-bromocyclohexene and *trans*-2-bromocyclohexanol also being formed. Additionally, in the HBr-catalysed reactions, substantial quantities of bromocyclohexane were found in the reaction products.

Results

The results are summarised in Tables 1—3. Corrections were applied, as described in Part 1,[1] in calculating the rate constants shown in Tables 2 and 3. The corrections would have been difficult to apply to the less accurate results shown in Table 1 and were omitted.

Discussion

The reactions catalysed by hydrogen bromide were shown to be of first order in bromine by the order plots $\{\log(-d[Br_2]/dt)$ *versus* $\log [Br_2]\}$ in individual reactions. Figure 1 is a first-order plot of the disappearance of bromine (63 points, ρ 0.999 91, 56% of reaction followed). When $[C_6H_{10}]$ was varied, the reaction appeared to be first order in that component, although this was not tested thoroughly. When [HBr] was varied, a rough proportionality to [HBr] was observed, but it appeared that cells that had formerly been used for this work retained enough hydrogen bromide to give a first-order process, despite careful washing with dry CCl_4. They probably contained $(0.5—1.5) \times 10^{-3}$M more hydrogen bromide than had been added. Water (always in much lower concentration than HBr) could not be varied, because unless its concentration was kept very low, microheterogeneity was evidenced by very irregular reactions. The poor reproducibility caused in part by adsorption of hydrogen bromide discouraged further investigation of the effect of initial bromine concentration or temperature, but the results of Table 1 suffice to confirm the reality of hydrogen bromide catalysis, and to indicate that a molecule of HBr is about five times as effective as one of Br_2 in catalysing the $C_6H_{10} + Br_2$ reaction. Very probably the bromine present also catalysed the addition of

Table 1. HBr-catalysed reactions

Run no.	$10^3[Br_2]$/M	$10^3[C_6H_{10}]$/M	$10^3[H_2O]$/M	$10^3[HBr]$/M	Temp. (°C)	% of Reaction followed	Order in Br_2 [a]	Pseudo-first-order [b] rate constant (10^3 s^{-1})	Third-order rate constant (l^2 mol^{-2} s^{-1})
371 [c]	5.49	118.4	0.7	10.0	24.9	63	1.10	11.4	9.6
372 [c]	5.49	138.1	0.7	10.0	24.9	56	1.05	14.1	10.2
373 [c]	5.49	157.8	0.7	10.0	24.9	48	1.15	14.7	9.3
374 [c]	5.49	177.6	0.7	10.0	24.9	41	0.95	25.4	14.3
375 [c]	5.49	197.3	0.7	10.0	24.9	38	1.00	16.9	8.6
360 [d]	3.89	59.2	0.7	9.7	24.9	66	0.85	9.3 (8.3) [e]	16.2
361 [d]	3.89	59.2	0.7	7.6	24.9	60	1.00	7.0 (6.0) [e]	15.6
362 [d]	3.89	59.2	0.7	6.0	24.9	75		4.1 (3.1) [e]	11.6
363 [d]	3.89	59.2	0.7	3.4	24.9	76	0.95	4.0 (3.0) [e]	20.0
364 [d]	3.89	59.2	0.7	1.7	24.9	83	1.05	2.4 (1.4) [e]	23.3
368 [d]	3.89	59.2	0.7	0	24.9	59	0.90	1.0 (0) [e]	∞

[a] Values are quoted to the nearest 0.05 when at least 30 data points were used. Standard errors in the values of the order in Br_2 range from 1.4—4.2% for the runs listed. [b] Standard errors in the values of the slopes of the first-order plots (from which the pseudo-first-order rate constants were obtained) range from 0.2 to 2.1% (for runs 360—368) and 0.2 to 0.4% (for runs 371—375). [c] Runs 371—375. Order in C_6H_{10} 1.11 ± 0.56. Third-order rate constant 11.3 ± 0.7 l^2 mol^{-2} s^{-1}. [d] Runs 360—368. Order in HBr 0.96 ± 0.18. Third-order rate constant 13.9 ± 2.7 l^2 mol^{-2} s^{-1}. [e] In runs 360—364, log [HBr] was plotted against log [$k_1' - {}_0k_1'$] to determine the order in HBr, where k_1' was the pseudo-first-order rate constant, and ${}_0k_1'$ was the pseudo-first-order rate constant for the reaction in which no HBr was added, *i.e.* run 368. This procedure gave a negligible intercept; if instead log [HBr] was simply plotted against log k_1' the order in HBr (slope) was 0.71 ± 0.15 but there was a significant intercept. It is assumed that run 368 was affected by HBr adsorbed on cell walls: compare the order of reaction (0.9) with runs 450—457.

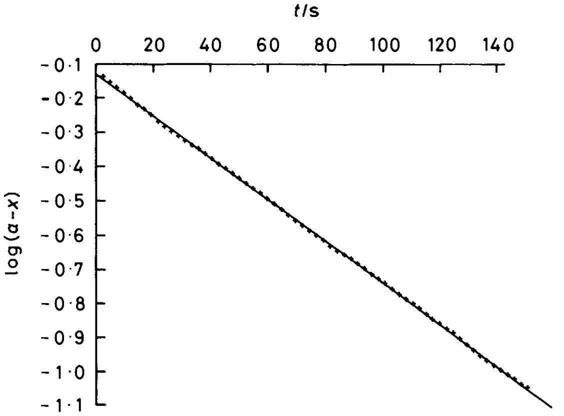


Figure 1. HBr-catalysed reaction. First-order plot of disappearance of bromine. 63 points, ρ 0.999 91, 56% of reaction followed. Points experimental, line computer-drawn

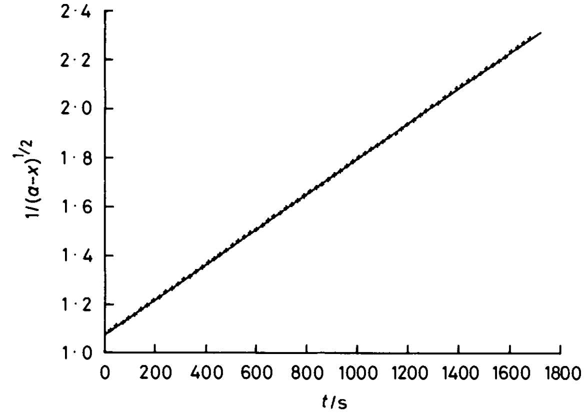


Figure 2. Reaction in absence of additives. 1.5-Order plot of disappearance of bromine. 70 points, ρ 0.999 97, 75% of reaction followed. Points experimental, line computer-drawn

HBr, but this reaction was not, to judge by product analyses, the major one (and of course is not measured: we studied Br_2 uptake).

If bromination by the ' Br_4' and ' HBr_3' mechanisms were the only important processes, we should expect that the former would begin to affect the slope of the order plots at very low HBr concentrations; it is difficult to make precise predictions because some HBr is formed in the ' Br_4' process (see Part 1[1]). This should lead to curved order plots from initially slow but autocatalytic reactions. These were not usually obtained. Instead, omission of added HBr led to runs like 385—390 (executed shortly after the HBr catalysis work) and 431—439 (executed after much further washing of the cells). The former set, intended to verify that the reaction is first order in cyclohexene, is probably more important as an example of the effect of adsorbed acid catalyst, the rapid reactions having the character, first order in bromine, of the preliminary experiments, described in Part 1,[1] some of which did show autocatalysis. The latter set includes several runs which are very accurately of order 1.5 in bromine, and distinctly slower; Figure 2 (run 436) illustrates the precision with which this kinetic form fits the data (70 points, ρ 0.999 97, covering 75% of the reaction). Plainly, any other explanation, such as a mixture of first- and second-order processes,[3] must be inadequate. Rather than deal with these results further, we turn to runs 450—457, in which succinimide is added, with the aim of simulating, under more controlled conditions, Phase 2 of the NBS-scavenged reactions described in Part 1.[1] Here

Table 2. Reactions in the presence of added imides

Run no.	$10^3[Br_2]$/ M	$10^3[C_6H_{10}]$/ M	$10^3[H_2O]$/ M	10^3[imide]/ M	Temp. (°C)	% of reaction followed	Order in Br_2 [a]	Pseudo-1.5-order [b] rate constant ($l^{0.5}$ $mol^{-0.5}$ s^{-1})	2.5-order rate constant ($l^{1.5}$ $mol^{-1.5}$ s^{-1})	Third-order rate constant (l^2 mol^{-2} s^{-1})
449 [c]	5.32	98.65	0.5	0 (S)	25.4	65	1.45	0.023	0.24 (0)	
450 [c]	5.32	98.65	0.5	1.40 (S)	25.4	71	1.65	0.209	2.18 (1.94)	58 (52)
451 [c]	5.32	98.65	0.5	1.09 (S)	25.4	72	1.65	0.195	2.04 (1.80)	62 (55)
452 [c]	5.32	98.65	0.5	0.78 (S)	25.4	72	1.60	0.169	1.77 (1.53)	63 (55)
453 [c]	5.32	98.65	0.5	0.47 (S)	25.4	71	1.55	0.131	1.37 (1.13)	63 (52)
454 [c]	5.32	98.65	0.5	0.31 (S)	25.4	74	1.55	0.116	1.21 (0.97)	69 (55)
455 [c]	5.32	98.65	0.5	0.22 (S)	25.4	71	1.60	0.093	0.97 (0.73)	66 (49)
456 [c]	5.32	98.65	0.5	0.16 (S)	25.4	69	1.55	0.081	0.85 (0.61)	67 (48)
457 [c]	5.32	98.65	0.5	0.09 (S)	25.4	73	1.50	0.064	0.67 (0.43)	71 (45)
486 [d]	4.54	78.9	0.3	1.53 (P)	25.2	67	1.45	0.066	0.86 (0.67)	22 (17)
487 [d]	4.54	78.9	0.3	1.21 (P)	25.2	74	1.50	0.058	0.76 (0.57)	22 (16)
488 [d]	4.54	78.9	0.3	0.88 (P)	25.2	74	1.45	0.042	0.54 (0.35)	18 (12)
489 [d]	4.54	78.9	0.3	0.65 (P)	25.2	77	1.40	0.033	0.43 (0.24)	17 (9.4)
490 [d]	4.54	78.9	0.3	0.33 (P)	25.2	73	1.45	0.027	0.35 (0.16)	19 (8.8)
491 [d]	4.54	78.9	0.3	0.23 (P)	25.2	74	1.50	0.024	0.32 (0.13)	21 (8.6)
492 [d]	4.54	78.9	0.3	0.16 (P)	25.2	79	1.35	0.036	0.47 (0.28)	37 (22)
493 [d]	4.54	78.9	0.3	0.10 (P)	25.2	74	1.45	0.026	0.34 (0.15)	34 (15)
494 [d]	4.54	78.9	0.3	0.03 (P)	25.2	65	1.55	0.017	0.22 (0.03)	40 (5.5)
495 [d]	4.54	78.9	0.3	0 (P)	25.2	63	1.70	0.014	0.19 (0)	

[a] Standard errors in the values of the order in Br_2 lie in the range 1.0—2.9% for all the runs listed. The orders are quoted to the nearest 0.05 when at least 30 data points were used, otherwise to the nearest 0.1. [b] Standard errors in the values of the slopes of the 1.5-order plots (from which the pseudo-1.5-order rate constants were obtained) lie in the range 0.1—2.3% for all the runs listed. [c] Runs 449—457. (S) = succinimide. Order in succinimide 0.56 ± 0.02, obtained by plotting log $[k'_{1.5} - {}_0k'_{1.5}]$ *vs.* log [S], where $k'_{1.5}$ and ${}_0k'_{1.5}$ are the pseudo-1.5-order rate constants for runs 450—457 and 449 respectively. The $k_{2.5}$ values are the $k'_{1.5}$ rate constants divided by the cyclohexene concentrations; values in parentheses are corrected by subtracting the rate constant for run 449, where no succinimide was present. Third-order rate constants are $k_{2.5}$ values, uncorrected and (corrected) divided by $[\text{succinimide}]^{0.5}$. A plot of $(k_{2.5} - {}_0k_{2.5})$ against $[S]^{0.5}$ gave a good straight line with a slope of 56 ± 2 for the third-order rate constant, ρ 0.997, and an intercept of −0.07 ± 0.04. [d] Runs 486—495 (P) = phthalimide. Order in phthalimide 0.61 ± 0.11, obtained as in *c* using run 495 (no phthalimide present) for correction. $k_{2.5}$ and third-order rate constants obtained as in *c*. A plot of $(k_{2.5} - {}_0k_{2.5})$ against $[P]^{0.5}$ gave a straight line with a slope of 17 ± 3 for the third-order rate constant, ρ 0.911, and an intercept of −0.06 ± 0.07.

again, order plots for bromine approximate to 1.5, and rate constants calculated on this basis show a very satisfactory log/log plot against [succinimide] with a slope of 0.47 ± 0.02. We therefore need to find an explanation for the rate law, rate = $k_3[C_6H_{10}][Br_2]^{1.5}[S]^{0.5}$ (where S = succinimide). One attractive hypothesis is Scheme 1, in which we consider how reasonable equilibria might allow an explanation based on the now established HBr_3 reaction. Provided that HBr_3 is not largely formed from HBr and Br_2, Scheme 1 fits the observed rate law, but the rate constant for the HBr_3 reaction, determined as above, is *ca.* 10—100 times too low to allow equilibrium constants for steps 1 and 1a to be assigned and Scheme 1 to be fitted to our results. We must find another explanation, and we have one in Scheme 2, which we will call ' the HBr_5 reaction '. Here we must assume that HBr_5 *is* mainly formed, from the small amount of HBr derived from water or imide and the large excess of bromine; note that whereas molecular HBr_3 can have no stable structure, HBr_5 can represent the ion-pair $Br_3^+{\cdot}HBr_2^-$. Much work on the ' positive halogen ' species present in many efficient halogenating solutions shows them to contain Cl^+, Br^+, or I^+ covalently bonded to some abundant molecule, and Br_3^+ is well attested.[4]

Although Scheme 2 rationalises the observed orders of 1.5 for bromine, 1 for cyclohexene, and 0.5 for succinimide, it also implies an order of 0.5 in water. Our findings suggest (there is much scatter) a positive order in water in reactions without

Table 3. Reactions in the absence of additives

Run no.	$10^3[\mathrm{Br_2}]$/M	$10^3[\mathrm{C_6H_{10}}]$/M	$10^3[\mathrm{H_2O}]$/M	Temp. (°C)	% of reaction followed	Order in $\mathrm{Br_2}$ [a]	Pseudo-1.5-order [b] rate constant ($\mathrm{l^{0.5}\,mol^{-0.5}\,s^{-1}}$)	2.5-order rate constant ($\mathrm{l^{1.5}\,mol^{-1.5}\,s^{-1}}$)
385 [c]	4.15	78.9	~0.2	25.3	85	0.90 [d]	0.065 (2.4) [e]	0.85
386 [c]	4.15	98.65	~0.2	25.3	90	0.95 [d]	0.084 (2.7) [e]	0.88
387 [c]	4.15	118.4	~0.2	25.3	86	1.10 [d]	0.087 (2.9) [e]	0.76
388 [c]	4.15	138.1	~0.2	25.3	85	1.10 [d]	0.096 (3.0) [e]	0.72
389 [c]	4.15	157.8	~0.2	25.3	78	1.4	0.136	0.89
390 [c]	4.15	177.6	~0.2	25.3	83	1.4	0.141	0.82
431 [f]	4.12	78.9	0.3	25.3	73	1.55	0.020	0.27
433 [f]	4.12	78.9	0.8	25.3	77	1.50	0.023	0.30
434 [f]	4.12	78.9	0.7	25.3	79	1.60	0.025	0.33
435 [f]	4.12	78.9	0.6	25.3	74	1.45	0.023	0.30
436 [f]	4.12	78.9	0.5	25.3	75	1.50	0.021	0.28
437 [f]	4.12	78.9	0.4	25.3	76	1.45	0.021	0.27
438 [f]	4.12	78.9	0.4	25.3	76	1.35	0.021	0.27
439 [f]	4.12	78.9	0.3	25.3	70	1.45	0.017	0.22

[a] Standard errors in the values of the order in $\mathrm{Br_2}$ lie in the range 1.2—2.3% for all the runs listed. The orders are quoted to the nearest 0.05 when at least 30 data points were used, otherwise to the nearest 0.1. [b] Standard errors in the values of the slopes of the 1.5-order plots (from which the pseudo-1.5-order rate constants were obtained) lie in the range 0.1—2.7% for all the runs listed. [c] Runs 385—390. Order in $\mathrm{C_6H_{10}}$ 0.94 ± 0.14. 2.5-order rate constant 0.81 ± 0.12 $\mathrm{l^{1.5}\,mol^{-1.5}\,s^{-1}}$. [d] Runs 385—388. These reactions were performed shortly after the HBr-catalysed runs 371—375 (Table 1), and are clearly first-order in $\mathrm{Br_2}$, not of order 1.5. We are almost certainly observing the effect of HBr adsorbed on the cell walls in these runs (see footnote *e* to Table 1). [e] The figures in parentheses are the pseudo-first-order rate constants ($\times 10^3$) for these reactions (*cf.* the values for runs 360—368 in Table 1). [f] Runs 431—439. Order in $\mathrm{H_2O}$ 0.27 ± 0.06.

$$\left.\begin{array}{lrcl}
1 & \mathrm{Br_2 + H_2O} & \rightleftharpoons & \mathrm{HBr + HOBr} \\
1a & \mathrm{Br_2 + C_4H_4O_2NH} & \rightleftharpoons & \mathrm{HBr + C_4H_4O_2NBr}
\end{array}\right\}
\begin{array}{l}
\text{fast, leading to} \\
[\mathrm{HBr}] = K[\mathrm{Br_2}]^{0{\cdot}5}[\mathrm{H_2O}]^{0{\cdot}5} \\
\text{or } K'[\mathrm{Br_2}]^{0{\cdot}5}[\mathrm{C_4H_4O_2NH}]^{0{\cdot}5}
\end{array}$$

$$2 \qquad \mathrm{HBr + Br_2 + C_6H_{10}} \xrightarrow{\text{slow}} \text{products; rate} = k[\mathrm{HBr}][\mathrm{Br_2}][\mathrm{C_6H_{10}}]$$

Scheme 1.

$$\left.\begin{array}{lrcl}
3 & \mathrm{3Br_2 + H_2O} & \rightleftharpoons & \mathrm{HBr_5 + HOBr} \\
3a & \mathrm{3Br_2 + C_4H_4O_2NH} & \rightleftharpoons & \mathrm{HBr_5 + C_4H_4ONBr} \\
3b & \mathrm{3Br_2 + C_8H_4O_2NH} & \rightleftharpoons & \mathrm{HBr_5 + C_8H_4O_2NBr}
\end{array}\right\}
\begin{array}{l}
\text{rapid, giving} \\
[\mathrm{HBr_5}] = K[\mathrm{Br_2}]^{1{\cdot}5}[\mathrm{H_2O}]^{0{\cdot}5} \\
\text{or } K'[\mathrm{Br_2}]^{1{\cdot}5}[\mathrm{C_4H_4O_2NH}]^{0{\cdot}5} \\
\text{or } K''[\mathrm{Br_2}]^{1{\cdot}5}[\mathrm{C_8H_4O_2NH}]^{0{\cdot}5}
\end{array}$$

$$4 \qquad \mathrm{HBr_5 + C_6H_{10}} \longrightarrow \text{products}$$

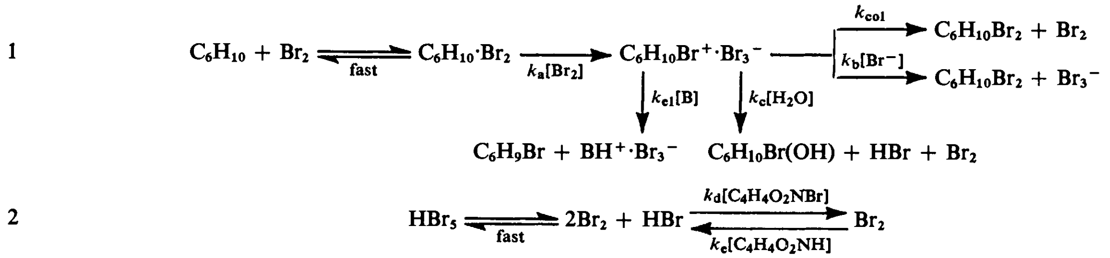
Scheme 2.

additives, but it is 0.27 ± 0.06 rather than 0.5. A value lower than 0.5 would be expected if water, which in pure $\mathrm{CCl_4}$ is mainly monomeric,[5] were present in these solutions containing bromine and cyclohexene partly or mainly in an effective dimeric or trimeric form. (However, equilibria involving the formation of HOBr would not explain our results, as the order in bromine would then change.) Equilibrium 3 is thus less well supported than 3a and our belief that reactions in solutions containing no additive involve attack by $\mathrm{Br_3^+{\cdot}HBr_2^-}$ on cyclohexene as the main component depends to some extent on analogy with the imide-catalysed reactions.

The validity of our views that NBS acts merely as a scavenger for HBr was confirmed by the substitution of *N*-bromophthalimide, when kinetic order and rate for the $\mathrm{Br_4}$ process were unaltered (Part 1 [1]). When phthalimide was substituted for succinimide, again the expected result was obtained. The kinetic order in bromine was unchanged at 1.5, and the rate was again proportional to $[\text{imide}]^{0{\cdot}5}$ (experimentally, the order was 0.61 ± 0.11), but the rate constant was *not* the same. There is no reason why it should be; equilibrium 3b will not have the same constant as equilibrium 3a. In fact, phthalimide was only some 30% as effective as succinimide in generating $\mathrm{HBr_5}$, so that the water term from (3), not under full control, was relatively more important and there was more scatter from run to run. Individual runs, however, obeyed the 1.5 order rate law very precisely, as Figure 3 (70 points, ρ 0.999 98, 74% of the reaction followed) illustrates.

When no imide was added, poor reproducibility was a major problem, and our choice of runs 431—439 is undeniably selective; there are, however, others giving quite similar results, including 449 and 495.

As well as explaining observed orders of reaction and allow-



Scheme 3. Similar equilibria for other bromide-ion donors

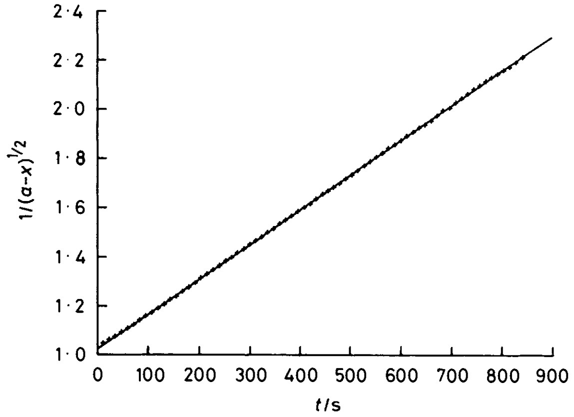


Figure 3. Reaction in presence of added phthalimide. 1.5-Order plot of disappearance of bromine. 70 points, ρ 0.999 98, 74% of reaction followed. Points experimental, line computer-drawn

ing the assignment of a self-consistent set of rate constants, a mechanistic picture must account for the transition from one kinetic form to another as conditions change. In an experiment typical of Part 1, we begin with $[C_6H_{10}]$ 10^{-1}M, $[Br_2]$ 10^{-3}M, and $[C_6H_{10}\cdot Br_2]$ appreciable but less than 10^{-3}M, say, for the sake of illustration, 10^{-4}M. Each Lewis acid (acceptor of Br^-) can react with the molecular complex, and each electrophile (donor of Br^+) can react with the hydrocarbon, so that the rate of formation of species $C_6H_{10}Br^+\cdot X^-$ is the sum of two sets of reactions. We argue that the term from $C_6H_{10}\cdot Br_2 + Br_2$ dominates the process. This implies that the term from $C_6H_{10}\cdot Br_2 + HBr$ is unimportant, therefore [HBr] $<10^{-5}$, since the corresponding rate constant is five times as large. The term from $Br_3^+\cdot HBr_2^- + C_6H_{10}$ is also smaller, and the concentration of this electrophile must therefore be very small, since this reaction has a large rate-constant. Consider a simplified scheme for the whole reaction (Scheme 3). Here, k_b and k_{el} are composite, the former multiplying various bromide-ion donors, the latter various bases.

Initially the bromonium tribromide, formed in the rate-determining step proportional to $[C_6H_{10}][Br_2]^2$, partitions between collapse and reaction with external nucleophiles, initially only H_2O. Significant amounts of HBr form, in this way and by elimination, and regenerate Br_2 with the consumption of NBS in reaction 2. Assuming equilibrium 3a, $[Br_3^+\cdot HBr_2]$ will be proportional to $[Br_2]^3$[succinimide][NBS]$^{-1}$, so long as appreciable amounts of NBS survive, and on our hypothesis the equilibrium constant k_d/k_e is so low that despite a large rate coefficient the term multiplying $[Br_3^+\cdot HBr_2^-]$ by $[C_6H_{10}]$ will be small compared with $k_a[C_6H_{10}\cdot Br_2][Br_2]$. But the consumption of NBS is zero-order in NBS, as long as the reaction k_d[NBS] is faster than the processes forming HBr. When the concentration of NBS has fallen to some level, say 10^{-6}M, this ceases to be true, and the concentration of HBr and all species proportional to it, including HBr_5, rises through several powers of ten, in a period, say, between 99 and 99.9999% of the consumption of NBS. After a transition lasting only a second, or thereabouts, in which dramatic autocatalysis occurs, the concentration of NBS will become steady at a value (say 10^{-8}M) determined by equilibrium 3a, $[Br_3^+\cdot HBr_2^-]$ will be, say, 10^5 times larger than at the beginning of the reaction, and the term $k_f[C_6H_{10}][HBr_5]$ will dominate the bromination.

During Phase 2, this main reaction will be accompanied by other processes. The Br_4 reaction will continue; calculation shows that it should contribute 3—11% of the reaction at the midpoint of typical succinimide-catalysed runs in Table 2, and a comparable amount in Phase 2 of the NBS-scavenged runs of Part 1. The HBr_3 process also is bound to occur, although not enough is known to calculate how much. The products of the former include bromo-alcohol and bromocyclohexene; the products of the main (HBr_5) reaction are unknown, but also probably include these compounds, and some HBr is therefore bound to be formed, although probably much less than the 0.02—0.06 mole per mole dibromide in the whole of Phase 1, including its initial part. The products of the ' HBr-catalysed bromination ' include significant amounts of bromocyclohexane, and this should therefore be considered as a composite of two reactions and almost certainly is a net consumer of HBr. Negative feedback should therefore occur among the side-reactions, the concentration of HBr and other species related to it thus being kept steady through the reaction. When only water is available to maintain $[HBr_5]$ constant *via* equilibrium 3, this steady state is not very robust and autocatalysis is sometimes observed, but the imide-catalysed runs and Phase 2 of the scavenged runs are well behaved, autocatalysis being undetectable. We are grateful to a referee for pointing out the need to justify the fact that autocatalysis is ever avoided; this is indeed necessary if our explanations are to be credible. We do not claim that they are fully proved, or that they are complete. In the HBr-catalysed runs (Table 1), for example, calculation implies that at the reaction mid-point 2—5% of the bromination involves the Br_4 process, and the HBr_5 process must also make some contribution. It is quite probable that water, by tying up HBr as $H_3O^+\cdot Br^-$, may inhibit the HBr_3 process. Again, we have no evidence for any homolytic chain reaction except during illumination, but this may only be true while inhibitors, *e.g.* O_2, maintain an induction period.

So far, we have considered the succinimide-catalysed runs as equivalent to Phase 2 of the scavenged runs. In the latter, the order in Br_2 was 1.5, and in ' consumed NBS ' 0.73 ± 0.10. These values compare reasonably well with those observed for the succinimide-catalysed processes, and the third-order rate constants are also in reasonable agreement [ranging from 46—121 (see Table 2, Part 1 [1]) to 42—53, measured directly]. For NBP-scavenged reactions, however, the rate in Phase 2 was much more sensitive to ' consumed NBP ' (orders 1.70 ± 0.07 and 1.33 ± 0.11, in two blocks of runs) than measured rates are to phthalimide (0.61 ± 0.11 in runs 486—495), and also much faster at fairly high initial NBP concentrations than would be expected on the basis of phthalimide presumably produced. We did not understand this, and it is mainly for this reason that we delayed publication in the hope of finding an explanation. It is, however, an anomaly of an explicable type; evidently the reaction of hydrogen bromide with NBP gives, in addition to phthalimide, another product which (a) is formed from two or more moles of NBP, and (b) takes part in an equilibrium of type (3), with an equilibrium constant which favours HBr_5 more than does (3a), and much more than (3b). It is not obvious what such a compound would be. Nevertheless, a reaction was carried out under conditions similar to NBP-scavenged kinetic runs, but on a larger scale. The main products were obviously dibromocyclohexane and phthalimide, but when the residue, after removal of volatile material, was examined mass spectroscopically, a signal at 292 a.u., with an intensity *ca.* 4% of the 147 a.u. phthalimide signal, was the strongest peak above 150 a.u. This corresponds to 2(phthalimide) − 2H; peaks corresponding to loss of CO (264) and CO and H_2O (246) from the 292 species were the two strongest signals between 150 and 292 a.u., so that recognition of this last as a molecular ion is not unreasonable. (There was, however, also a weaker signal at 326 a.u. which we do not understand, and is probably unrelated.) Any molecule formed from NBP (two molecules) would, if capable of reacting reversibly with bromine to give HBr_5 with an equilibrium constant more favourable than that in reaction (3b), explain our results in Phase 2 of the NBP-scavenged process. Biphenyltetracarboxylic di-imides, *N*-phthalimidophthalimides, and compounds in which one molecule of NBP has undergone a process equivalent to the NBP $\longrightarrow$ *o*-carboxyphenyl isocyanate reaction before reacting with phthalimide are all possible, although none is particularly plausible.

The smaller tendency for Phase 2 of NBS-scavenged reactions to show higher rates than succinimide-catalysed processes, and a larger (0.73 ± 0.10) order in 'consumed NBS' may have a similar explanation. It will be recalled (Part 1 [1]) that the consumption of NBS exceeded that calculated on the basis $C_4H_4O_2NBr + HBr \longrightarrow C_4H_4O_2NH + Br_2$, and that material less soluble than succinimide was formed. All four phenomena could have a common cause, if the reaction of NBS with gradually formed HBr gave one or more products other than succinimide, with the consumption of more than one molecule of NBS per molecule of HBr. However, this and the similar behaviour of NBP are peripheral to our interest in the bromination of cyclohexene.

Finally, we should ask what happens when bromine is added to cyclohexene in CCl_4 with no especial precautions. If the solvent has not been dried, the early stages of the reaction will form enough hydrogen bromide, as a by-product to the processes giving bromocyclohexene and the bromohydrin, to cause an aqueous phase to separate, and most of the reaction will take place in that phase. If solvent and reagents have been dried carefully, and no HBr is present, the residual water will allow reaction, order 1.5 in bromine, through HBr_5 to make the major contribution (*i.e.* attack of $Br_3^+{\cdot}HBr_2^-$ on olefin, initially giving $C_6H_{10}Br^+{\cdot}HBr_2^-$ and Br_2). If the bromine concentration is very high, contributions from Br_6 (and higher) aggregates may be important even in the absence of a scavenger. If the bromine contains much hydrogen bromide, the HBr_3 reaction (HBr catalysis of the conversion of charge-transfer complex to salt of bromonium ion) may be dominant. The rather slow process involving Br_4, probably the result of attack by Br_2 on the charge-transfer complex initially giving $C_6H_{10}Br^+{\cdot}Br_3^-$, is unlikely to be significant in the absence of a scavenger for hydrogen bromide; and the simplest reaction of all, $C_6H_{10} + Br_2 \longrightarrow C_6H_{10}Br_2$, (a) has never been shown to happen, and (b) has been shown *not* to be significant at bromine concentrations above 0.001M (Part 1 [1]), in the presence of a scavenger. The moral of the whole story is that if ionic reactions are carried out in non-polar media they may not be simple in kinetic form, and the negative overall enthalpy of activation demonstrated for the Br_4 process may be a commonplace feature. Although difficult to isolate and to investigate, such reactions may be discriminating and useful synthetically.

It will be appreciated that our account of the reaction between bromine and cyclohexene in carbon tetrachloride differs appreciably from that given by Fukuzumi and Kochi,[3] in a comparison between the bromination and the mercuration of several olefins. They found that molecular complexes were formed rapidly and reversibly; we had not done so, although we had suspected it and have now confirmed their findings. They considered that addition reactions first- and second-order in bromine occurred, but their rates for the former exceed the upper limits of possible reactions in the presence of NBS scavenger. Probably their reactions were similar to ours in the absence of additives, in which we believe that water plays an important role, and the main process is of order 1.5 (this can, of course, simulate a mixture of first- and second-order reactions).

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