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Occam's Razor Revisited. Chain Carriers in the N-Bromosuccinimide Bromination of Neopentane–Methylene Chloride[1]

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Abstract: Product analysis of neopentane–CH_2Cl_3 brominations by 200-MHz NMR and gas chromatography show that β-bromopropionyl isocyanate (BPI) is formed in all reactions, including those in the presence of added Br_2. Similarly a high yield of iodoisocyanate is formed in N-iodosuccinimide–I_2 reactions. In most experiments comparisons of BPI yields and neopentane/CH_2Cl_2 reactivities (r's) are reasonably consistent with competing succinimide radical (S·) and Br· chains although some experiments imply the existence of a second, non-BPI-producing chain carrier. Published data are reviewed, and it is concluded that all data which are reliable are now consistent with competing S·–Br· chains in which S· has the properties which have been ascribed to "S_σ·". In the presence of substrates with weak C–H bonds, Br· chains predominate, and are not entirely eliminated even by olefins as Br· traps. All attempts to demonstrate a third chain carrier clearly identified as another state of the succinimide radical now are unconvincing, and the hypothesis of two reactive states of S· is at best unnecessary.

The free radical chain nature of N-bromosuccinimide (NBS) brominations has been recognized since the 1940's, but the details of its mechanism have been the subject of recurrent controversy. By the mid 70's two reaction paths had been clearly recognized. One was a bromine atom chain (the Goldfinger mechanism) in which NBS acts merely as a Br_2 source, most easily observed with reactive substrates with allylic and benzylic hydrogen, preferably in solvents like CCl_4 in which NBS is only sparingly soluble (the conditions under which NBS is usually employed as a practical reagent). The other was a succinimide radical chain (the Bloomfield mechanism) important with unreactive substrates and most easily observed in the presence of olefins which could act as bromine or bromine atom traps and which was accompanied by a competing opening of the succinimide radical to yield β-bromopropionyl isocyanate (BPI). this story is well-known and has been frequently reviewed.[2-4]

In 1978 the subject was reopened by Skell and Day in two communications[5] and a review[2] in which they proposed that, actually, two succinimide radical chains exist, one involving the ground state, now identified as a π state[6] and designated S_π·, and the other an excited σ state S_σ·. Since 1982 this proposal has been elaborated in a series of further publications[7] and, in its present form, may be summarized as follows. The excited S_σ· is generated by an exothermic reaction between NBS and radicals forming strong C–Br bonds, e.g., primary and secondary radicals and ·$CHCl_2$. It shows a selectivity similar to Cl· and, by inference, reacts at similar rates. It adds readily to aromatic rings and it alone undergoes ring opening to yield BPI. Less exothermic reactions of NBS with, e.g., Br·, CCl_3·, and allyl radicals, produce S_π·, which shows a greater selectivity between substrates, does not add to aromatic rings, and does not open to yield BPI. Excited S_σ· is most reliably produced by conducting NBS brominations in the presence of an olefin lacking allylic hydrogen which acts as a Br· trap. Ground-state S_π· is produced in the presence of traces of Br_2 or, it is reported, relatively high concentrations of CCl_3Br or benzene.

In all the work reported from Skell's laboratory (comprising most of the data available) chain carriers, S_σ·, S_π·, and Br·, have been identified on the basis of product distributions, a well-established method in the study of radical chain reactions, since ratios of rate constants of competing chain propagation steps in general depend solely upon the nature of the chain carrying radicals and are independent of overall reaction rates, the nature

of chain initation, or the presence of trace impurities, inhibitors, etc. To date, succinimide radicals have not been detected under reaction conditions, and only one recent study of overall kinetics has been reported.[3]

The most carefully studied system has involved competitive bromination of neopentane–methylene chloride. Here Skell reports yields of BPI as high as 98% in the presence of olefins to scavenge bromine atoms and an r value (relative reactivities of neopentane:CH_2Cl_2 per H) of 17. If small amounts of Br_2 are added in the absence of olefin, r = 1.15 and no BPI is formed.[7a] In contrast, with Br_2 alone r = 0.06–0.1, at least under conditions where reversibility is unimportant.[5b,7d] These results have been qualitatively confirmed by Walling, El Taliawi, and Zhao,[3] although some significant differences are discussed below.

This paper describes a reexamination of the NBS–neopentane–CH_2Cl_2 and Br_2–neopentane–CH_2Cl_2 systems, employing what we consider a more sensitive and reliable analytical method for BPI in the former. We also present new data on N-iodosuccinimide reactions and attempt to evaluate the status of the whole problem in terms of two hypotheses: S_σ· and S_π· radicals or simply competing succinimide radical and bromine atom chains, as proposed previously for cyclopentane–cyclohexane bromination.[4]

Results

The NBS–Neopentane–$CHCl_2$ System. Since any interpretation of product distributions in terms of competing chains depends critically upon accurate and reliable product analyses, initial

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(2) Skell, P. S.; Day, J. C. Acc. Chem. Res. 1978, 11, 381. This and the following two references give leading references to the older literature.

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(6) An ESR spectrum attributed to the π state of the succinimide radical has been observed on 26 K irradiation of NBS crystals. Lund, A.; Samskog, P. O.; Eberson, L.; Lunell, S. J. Phys. Chem. 1982, 85, 2458.

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Table I. Photobromination of CH_2Cl_2–Neopentane by NBS in the Presence of Olefins[a]

[C₂H₄]	[CH₂Cl₂]	[C₅H₁₂]	% of reaction	products, mol/mol of NBS					r	Y (%)[d]
				BPI	NSH	C₂H₄Br₂	CHCl₂Br	C₅H₁₁Br		
0.011	15.3	0.186	80.0	0.71	0.051	0.024	0.024	0.034	17.8	92.7
0.011	15.3	0.186	82.0	0.71	0.067	0.027	0.028	0.038	18.3	91.5
0.011	15.3	0.186	77.0	0.71	0.024	0.025	0.024	0.031	17.9	92.8
0.0113	15.3	0.186	11.3	0.056	0.014	0.012	0.0013	0.0031	22.9	43.3
0.0113	15.3	0.186	51.2	0.37	0.13	0.014	0.016	0.015	12.8	92.3
0.0113	15.3	0.186	74.0	0.57	0.12	0.023	0.027	0.025	12.7	91.6
0.00086	12.5	1.72	100.0	0.53	0.41	0.0095	0.27	0.22	0.97	52.0
0.0002	12.7	1.59	17.6	0.039	0.043	tr[b]	0.0083	0.033	5.25	48.5
0.0002	12.7	1.59	28.5	0.076	0.098	tr	0.020	0.054	3.89	50.7
0.0002	12.7	1.59	56.9	0.22	0.36	tr	0.16	0.11	0.89	44.9
0.0002	12.7	1.59	65.8	0.26	0.43	tr	0.27	0.093	0.47	41.7
0.0002	12.71	1.59	100	0.19	0.81	tr	0.51	0.16	0.43	22.1
0.076[c]	15.0	0.38	20	0.05	0.09	0.0010	0.0020	0.006	19.7	81.8
0.076[c]	15.0	0.38	49	0.23	0.13	0.0022	0.0042	76	21.9	92.7
0.076[c]	15.0	0.38	85	0.39	0.12	0.0063	0.0114	0.032	18.5	90.0
0.076[c]	15.0	0.38	87	0.41	0.14	0.0071	0.0126	0.033	17.2	90.0

[a] All runs 0.1 M NBS, 15 °C, analysis by method A unless indicated (see Experimentl Section). [b] Trace too small for accurate measurement. [c] Vinylidene chloride, analysis by method B. [d] 100 × BPI/(BPI + CHCl₂Br + C₅H₁₁Br).
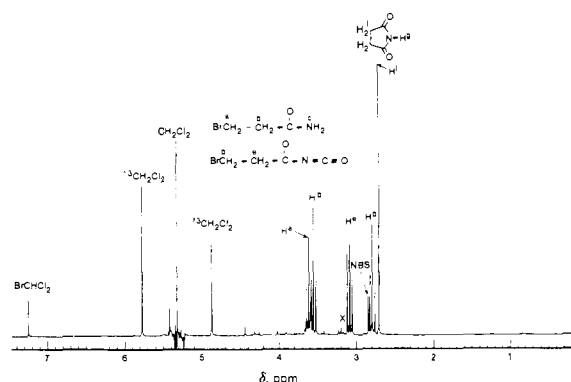

Figure 1. ¹H NMR spectrum (200 MHz) of the reaction product mixture from the photobromination of methylene chloride with NBS–vinylidene chloride (X = unknown).

Figure 2. ¹H NMR spectrum (200 MHz) of the reaction product mixture of Figure 1 after the addition of 1 µL of water (X = unknown).

discussion of this matter is in order. Yields of neopentyl bromide and $CHCl_2Br$, from which r's may be calculated, have previously been determined by gas–liquid chromatography (GLC) (or sometimes NMR). Since the products are stable and the techniques are straightforward and well established, we have employed them as well. On the other hand, BPI is relatively unstable and subject to rapid hydrolysis, either by traces of water in the reaction system or during subsequent manipulation.[8] In previous work, BPI has been detected qualitatively by its strong IR absorption peak at 2245 cm⁻¹ and quantitatively by 60-MHz proton NMR, integrating the area under the two characteristic triplets at δ 3.6 and 3.1. As discussed further below, this method has rather low sensitivity and either underestimates or fails to detect BPI which has undergone hydrolysis. In order to get around this difficulty, we have used two other complementary analytical methods.[9] In one, BPI is completely hydrolyzed to β-bromopropionamide (BPA) and determined by GLC. The importance of inadvertent hydrolysis as a complication became apparent when reaction mixtures were examined by 200-MHz proton NMR which resolves BPI and BPA. A typical result is shown in Figure 1. The downfield BPA triplet is just downfield from that of BPI, but the upfield triplet is shifted upfield to δ 2.8, between the singlets of succinimide and unreacted NBS. As Figure 2 shows, addition of a trace of water converts the mixture to pure BPA, confirming the identification. Accordingly, as an alternative analytical method, BPI has been determined by integration of the peaks around δ 3.6,

usually after addition of a little water to convert BPI to BPA and sharpen the spectra. With use of a 200-MHz FT Bruckner instrument with 48 repetitive scans, less than 1% BPI based on total NBS was detectable, and reaction mixtures analyzed by both methods agreed within 5% of measured values. For comparison with previous analytical techniques, Skell, using 60-MHz NMR with a Varian EM-360 instrument, reported a limit of detection for BPI of 0.09 mmol corresponding to 5% of the total NBS in typical experiments.[7a,10] At least in some cases, analyses were carried out on the volatile material separated by low-pressure distillation into a cold trap, so any BPA present would not be detected. In the earlier work at Utah,[3] NMR analyses were carried out on our total reaction mixtures, again with a EM-360 instrument. Reexamination of a number of spectra indicates that the integral of absorption peaks in the BPI region becomes significant and measurable at about 5% BPI based on initial NBS, but individual peaks are scarcely distinguishable from noise at 10% and could be missed at considerably higher concentrations if their presence was not anticipated. Further, with the aid of hindsight, it is evident that in many cases the peaks at δ 3.6 are larger than those at δ 3.1 (particularly at low conversion), indicating the presence of varying quantities of BPA.

Recently we have analyzed a number of runs at Utah by 300-MHz NMR and have confirmed these Alberta results. Both BPI and BPA are formed in typical reactions and can be detected

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(8) Previous workers have employed commercial NBS, either used as received or after recrystallization from water, and have not reported any unusually rigorous precautions to eliminate traces of moisture.[3,7]

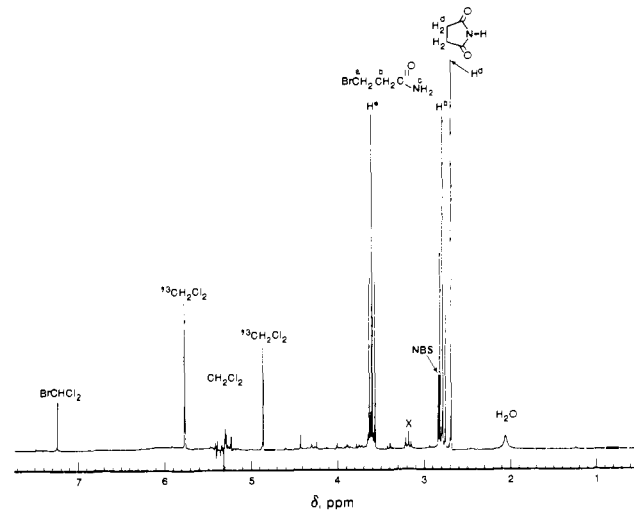(9) Unless indicated, all experiments reported here have been carried out at the University of Alberta.

(10) More recently[7d] Skell has restated his detection limit as 0.02 mol (by the same method) without explanation.

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Table II. Photobromination of CH$_2$Cl$_2$-Neopentane by NBS Alone[a]

% of reaction	products, mol/mol of NBS				r	Y (%)
	BPI	NSH	CHCl$_2$Br	C$_5$H$_{11}$Br		
13.3	0.042	0.088	0.015	0.016	1.44	57.5
18.3	0.059	0.17	0.038	0.029	1.03	46.8
23.6	0.096	0.13	0.046	0.033	0.965	54.9
33.1	0.074	0.20	0.12	0.046	0.517	32.2
39.8	0.13	0.19	0.17	0.056	0.432	36.5
49.8	0.13	0.32	0.22	0.046	0.276	32.8
97.1	0.17	0.74	0.71	0.074	0.138	17.8
100	0.17	0.73	0.81	0.077	0.127	16.1
100[b]	0.60		0.833	0.319	5.23	60

[a] All runs 0.104 M NBS, 12.7 M CH$_2$Cl$_2$, 1.56–1.61 M neopentane, 15 °C. Analyses by method A. [b] Run at Utah, NMR analysis.

even in runs in the presence of Br$_2$· (see below).

Results, using these methods of analysis, for the NBS–neopentane–CH$_2$Cl$_2$ system in the presence of ethylene as a Br· scavenger are shown in Table I. At 9:1 and 7.8:1 NBS–ethylene ratios we observe high BPI yields and large r's, although at 7.8:1 the latter drop somewhat with conversion. From the yields of ethylene dibromide, considerable ethylene is consumed, and, if it is assumed that each molecule of ethylene dibromide represents the trapping of a bromine atom generated by NBS photolysis, kinetic chain lengths are in the range 10–40. At 120:1 NBS–ethylene, r's are initially high but drop markedly with conversion. Ethylene dibromide yields indicate that essentially all the ethylene is gone at about 60% reaction. A series with even less ethylene gives still smaller decreasing r's, but still appreciable yields of BPI. A few runs with vinylidene chloride in place of ethylene give similar results.

In addition to the runs in Table I, several experiments were carried out at higher olefin concentrations, NBS:ethylene ~2. Here only traces of CHCl$_2$Br were detected along with substantial quantities of 1-bromo-3,3-dichloropropane. Under these conditions ·CHCl$_2$ radicals are evidently trapped by ethylene rather than reacting with NBS. We now believe that the same explanation accounts for the low CHCl$_2$Br yields reported by Walling[3] at relatively high concentrations of vinylidene chloride. Negligible amounts of C$_3$H$_5$Cl$_2$Br were detected in the runs in Table I.

In summary, while we do observe the product distribution ascribed by Skell to S$_\sigma$·, ethylene concentrations are rather critical. Too much traps ·CHCl$_2$ and gives high values of r; too little fails to trap Br· completely and is depleted during reaction.[3,7]

Table II presents a series of runs in the absence of olefin or another additive. Both r's and BPI yields decrease with conversion as Br$_2$ builds up in the system as would be anticipated from previous results.[4]

Table III shows our results in the presence of Br$_2$, which are quite different from previous reports. First, by our analytical methods *all runs show significant BPI* so the chain carier which produces it is not entirely eliminated. Second, *r's vary widely*, and we have failed to find a range of reagent concentrations duplicating Skell's S$_\pi$· conditions, r = 1.15 and no BPI, even though the last ten runs were intended to reproduce as exactly as possible the one previous experiment on this system described in detail.[11] Our conclusion is that mixed carrier chains must, in fact, occur under almost all conditions. Further, while there is a general trend of decreasing r's and BPI yields with increasing Br$_2$, r's vary considerably for essentially replicate experiments, so contributions from different carriers must vary in a so far unpredictable manner. While the results of all three tables do not immediately vitiate the S$_\pi$·–S$_\pi$· hypothesis, they require a more complex analysis to differentiate the relative contributions of the chain carriers involved and the appropriate r values associated with them.

Product Distributions from Competing Chains. If we consider the competitive simultaneous bromination of two substrates AH and BH (here neopentane and CH$_2$Cl$_2$, respectively) by some sort of succinimide radical S·, which can also open to yield BPI and
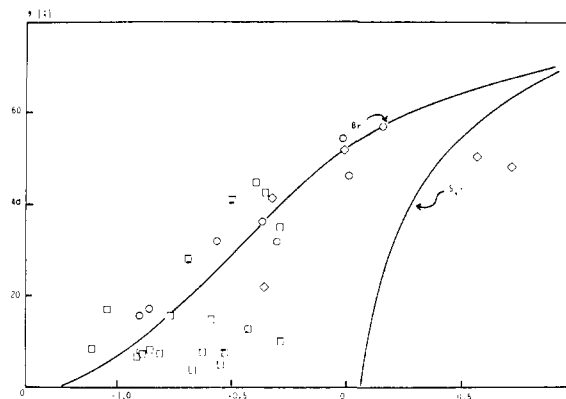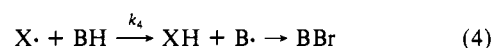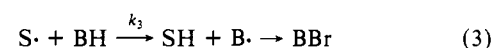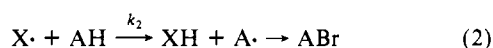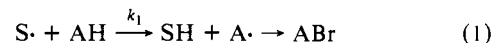
(11) Cf. ref 7a, p 7266.

Figure 3. Plot of BPI yield vs. log r for CH$_2$Cl$_2$-neopentane brominations. ◇, NBS + olefin; ○, NBS alone; □ NBS–Br$_2$. (Tables I–IV.)

another radical X·, which does not yield BPI, product distributions will be determined by five competing propagation steps:

$$S\cdot + AH \xrightarrow{k_1} SH + A\cdot \rightarrow ABr \tag{1}$$

$$X\cdot + AH \xrightarrow{k_2} XH + A\cdot \rightarrow ABr \tag{2}$$

$$S\cdot + BH \xrightarrow{k_3} SH + B\cdot \rightarrow BBr \tag{3}$$

$$X\cdot + BH \xrightarrow{k_4} XH + B\cdot \rightarrow BBr \tag{4}$$

$$S\cdot \xrightarrow{k_5} \cdot CH_2CH_2CONCO \rightarrow BPI \tag{5}$$

Exactly how S· and X· are interconverted is not relevant, and, if AH and BH concentrations do not change significantly during reaction and chains are reasonably long, the relation between the observed r and Y, the BPI yield (as the fraction of BPI + ABr and BBr),[12] is given by

$$r = \frac{(k_1/k_5)Q + (k_2/k_4)(1/Y - 1/Y_s)}{6(k_3/k_5)Q + 6(1/Y - 1/Y_s)} \tag{6}$$

where $Q = (k_2/k_4)[A] + [B]$ and Y_s is the BPI yield expected if S· were the sole chain carrier, i.e., $1/Y_s = (k_1/k_5)[A] + (k_3/k_5)[B] + 1$. A deviation of (6) is given in the Appendix and shows that *(6) is valid regardless of any variations in the relative contributions of S· and X· chains during the reaction.* This is important since in all probability the contributions do vary in high conversion experiments. The various rate constant ratios in (6) can be calculated from data from experiments under pure S· and X· conditions if these can be achieved. It will be noted that both Q and Y_s depend upon [A] and [B].

In the event that more than one X· species is involved (6) is still valid if k_2/k_4 is replaced by an "effective k_2/k_4", a sort of average of the contributions of the different X· species involved.[14] Accordingly (6) can be used either to identify X· if only one is present or, if the reaction is more complex, to calculate "effective k_2/k_4's" as a clue as to what is going on.

If we assume that the first and last four runs in Table I represent pure S· chains, we calculate k_1/k_5 = 0.234 ± 0.017, k_3/k_5 = 0.00205 ± 0.00017, and r_s = 19.3 ± 0.7 (errors are standard deviations of means). We can now check two hypotheses: that X· is Skell's S$_\pi$· (k_2/k_4 = 6 × 1.15 = 6.9) or that X· is actually Br· (k_2/k_4 = 6 × 0.056 = 0.336). Our choice of r_{Br} = 0.056 is discussed further below, but all measurements indicate it lies in the range 0.04–0.1. Figure 3 shows the data for all those runs in Tables I–III in which CH$_2$Cl$_2$ and neopentane were approximately 12.58 and 1.55 M, respectively,[13] so that constant values

(12) Since these are the only products accounted for by this reaction scheme, this is the proper "yield". However, it should be noted that in the tables material balances for Br are generally <100% so other bromine-containing products must be produced. This has been noted previously.[2]

Table III. Photobromination of CH_2Cl_2–Neopentane by NBS–Br_2[a]

[Br$_2$] $\times$ 10^2	% of reaction	products, mol/mol of NBS				r	Y (%)
		BPI	NSH	CHCl$_2$Br	C$_5$H$_{11}$Br		
0.09	30.0	0.040	0.26	0.19	0.027	0.172	15.6
0.09	98.8	0.13	0.87	0.61	0.13	0.258	14.9
0.10	43.0	0.12	0.27	0.11		0.407	44.9
0.10	46.0	0.14	0.31	0.16	0.042	0.318	40.9
0.10	72.3	0.18	0.55	0.42	0.071	0.205	26.8
0.10	78.6	0.32	0.48	0.32	0.112	0.454	42.1
0.11	100	0.083	0.82	0.44	0.23	0.516	9.7
0.11	100	0.064	0.85	0.62	0.15	0.293	7.7
0.13	15.3	0.008	0.15	0.086	0.011	0.157	7.6
0.13	100	0.15	0.85	0.77	0.24	0.377	12.9
0.15	47.4	0.10	0.29	0.13	0.056	0.522	35.0
0.15	32.6	0.044	0.40	0.20	0.015	0.091	17.0
0.15	29.9	0.024	0.29	0.25	0.016	0.078	8.3
0.23	92.2	0.078	0.92	0.79	0.092	0.141	8.1
0.23	94.7	0.079	0.92	0.88	0.095	0.131	7.5
0.23	96.6	0.073	0.93	0.78	0.084	0.130	7.8
0.43	54	0.031	0.45	0.36	0.037	0.125	7.3
0.43	63	0.045	0.59	0.44	0.087	0.240	7.9
2.12	76	0.037	0.76	0.59	0.14	0.287	4.8
2.12	96	0.039	0.99	0.85	0.15	0.214	3.8
0.03[b]	100	0.067		0.77	0.17	0.130	6.7
0.017[c]	13.5	0.0032	0.046	0.121	0.041	0.169	1.9
0.017[c]	14.4	0.0041	0.070	0.134	0.038	0.137	2.3
0.017[c]	21.0	0.0072	0.058	0.152	0.050	0.123	3.4
0.017[c]	25.8	0.0062	0.068	0.134	0.037	0.155	3.5
0.017[c]	60.0	0.026	0.515	0.248	0.178	0.415	5.8
0.017[c]	82.8	0.034	0.701	0.279	0.285	0.591	5.7
0.017[c]	89.7	0.051	0.60	0.234	0.289	0.718	8.9
0.02[b,c]	70	0.088		0.263	0.350	0.79	12.5
0.02[b,c]	100	0.113		0.29	0.59	1.26	11.3
0.02[b,c]	100	0.075		0.30	0.63	1.11	7.5

[a] Unless indicated, [NBS] = 0.1 M, [CH$_2$Cl$_2$] = 12.5 M, and neopentane = 1.72 M; analysis by methods A and B. [b] Experiments at Utah. NMR analyses. [c] These experiments under heterogeneous conditions, [NBS] = 0.4 (total). [CH$_2$Cl$_2$] = 10.26 M, [neopentane] = 2.92 M. Analysis by method C.

of Q and Y_s should apply, together with curves calculated from the parameters just cited. A log r scale is used to spread out small values of r (r's vary by a factor of over 200) and because experimental uncertainties in r's are approximately proportioned to measured values.

Clearly the assumption of competing $S_\sigma\cdot$ and $S_\pi\cdot$ chains is not supported. Rather the experimental points (with the exception of six which deviate rather badly) are scattered about the S$\cdot$–Br$\cdot$ line with a median deviation of log r of approximately 0.1 log unit. This is larger than would be expected if we assume a 5% uncertainty (standard deviation) in the actual measurement of BPI and alkyl bromides (which would give a 0.03 standard deviation in log r and a similar but more variable spread in Y). However, experience shows that a series of measurements made in the same laboratory over a period of time on systems where only a single-chain carrier is believed to be involved show a wider spread in r's than this so that additional systematic errors must be involved. Thus Skell has reported "r_σ" values of individual experiments ranging from 23 to 15[5b,7a] (standard deviation log r = 0.057), and our own data from Table I show a similar spread. Even larger spreads in individual measurements of r_{Br} have been observed in several laboratories (see below).

Although Figure 3 gives a good visual presentation of the actual data and provides a basis for identifying "X$\cdot$," a better test for goodness of fit is provided by a plot of log r_{obsd} vs. log r_{calcd} (or Y_{obsd} vs. Y_{calcd}) since now all data (involving varying neopentane concentrations) can be employed. Such a plot, assuming Br$\cdot$ as the other chain carrier, is shown in Figure 4, together with a linear least-squares fit to the data, excluding about 30% of the points enclosed by the dashed line. The slope of the line is 1.01, indistinguishable from unity, with a correlation coefficient of 0.97 and a median deviation of points from the line of again approximately 0.1 log unit.
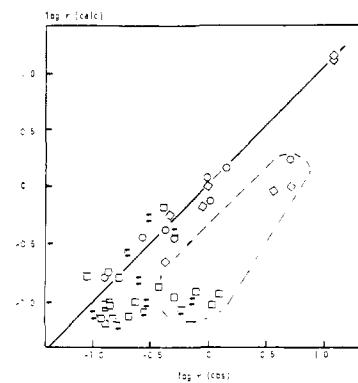

Figure 4. Plot of log r(calcd) vs. log r(obsd), assuming competing S$\cdot$ and Br$\cdot$ chains (same symbols as Figure 3).

With this said, we are still left with the problem of the deviant points. The data of Tables I–III include essentially all the experiments which gave enough of all products for accurate analysis and which were carried out since our analytical methods were perfected. If we resist the temptation to discard these deviat points as simply representing occasional bad experiments, we must conclude that under some conditions the NBS–CH$_2$Cl$_2$–neopentane system behaves as though the non-BPI-producing chain carrier or carriers X$\cdot$ are characterized by r values greater than 0.056, although the data are fitted by no single r value, nor tell us much immediately about the nature of X$\cdot$.[14] We will return to this matter in our discussion.

The Br$_2$–CH$_2$Cl$_2$–Neopentane System. Although there is now reasonable agreement as to the approximate value of r_{Br} for

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(13) Corresponding to 31.2 mmol of CH$_2$Cl$_2$ and 3.9–4.4 mmol of neopentane. 4.1 mmol = 1.55 M.

(14) As shown in the Appendix, for a series of X$\cdot$ radicals this "effective k_2/k_4" is actually $\sum k_{2i} \int [X_i] \, dt / \sum k_{4i} \int [X_i] \, dt$. Since the integrals are not known and presumably vary for each experiment the k_{2i}/k_{4i}'s cannot be determined although the "effective k_2/k_4" (and an associated effective r_x) can be calculated from (6) for each experiment.

**Table IV.** Photoiodination of CH_2Cl_2–Neopentane by NIS–I_2[a]

[I$_2$]	% of reaction	products (%)[b]				
		IPI	NSH	CHCl$_2$I	C$_5$H$_{11}$I	r
0.0046	51–90	75.0 ± 3.4	25.1 ± 3.4	7.66 ± 0.34	4.69 ± 0.11	0.72 ± 0.02 (2)[c]
0.0022	61–79	72.6 ± 2.5	27.4 ± 2.5	7.46 ± 1.65	4.84 ± 0.76	0.78 ± 0.05 (3)[c]

[a] NIS 0.046–0.051 M, CH_2Cl_2 12.4 M, neopentane 1.72–1.76 M, 15 °C.   [b] As % of NIS reacted (analysis by NMR and GLC).   [c] Number of experiments.

neopentane–CH_2Cl_2, the significance of possible reversibility of hydrogen abstraction due to HBr formed during the reaction has not been entirely resolved. Skell originally reported $r = 0.1$ without experimental details,[5b] but more recently[7d] has described three experiments in the presence of K_2CO_3 as an HBr trap giving $r = 0.057 ± 003$ (all experimental errors are mean standard deviations) and a single run (9% conversion) without K_2CO_3 $r = 0.39$. Walling[3] has reported ten measurements without HBr traps carried to 3–88% conversion giving $r = 0.048 ± 0.009$ and including a set of five on a single reaction (followed by NMR from 26% to 77% reaction) which showed a moderate decline in r with conversion. We have now carried out 5 runs (0.1–0.5 M Br_2, 4–15% reaction) giving $r = 0.056 ± 0.005$, and this is the value used in our calculations. Higher Br_2 concentrations gave slightly higher r's while in the gas phase at very low conversion (0.5–1.5%) 3 runs gave $r = 0.037 ± 002$. Our new data appear in Table V. With the exception of Skell's single high value, all results are now in reasonable agreement and indicate that reversibility does not significantly perturb measured r values, at least for runs below 50% conversion.

We have also probed the importance of reversibility directly by brominating a mixture of CD_2Cl_2 and neopentane with 1:1 Br_2–HBr. Analysis of recovered CD_2Cl_2 showed an amount of $CHDCl_2$ corresponding to not more than one R· + HBr reaction per 4 molecules of brominated product produced.

Actually, the prior literature provides considerable information on this reversibility problem. The reaction involved is

$$Br· + RH \underset{k_{-a}}{\overset{k_a}{\rightleftharpoons}} HBr + R· \overset{Br_2}{\underset{k_b}{\longrightarrow}} RBr + Br· \qquad (7)$$
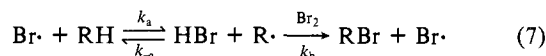
and the importance of reversibility depends upon [HBr]/[Br_2] and the reversibility ratio $n = k_{-a}/k_b$. The equation predicting the effect of reversibility on measured r's in competitive reactions was first worked out for the kinetically equivalent case of reversible thiol additions to olefins[15] and has been applied to brominations by Tanner[16] and by Zavitsas.[17] The equation shows that measured r's are perturbed from their true values only if n's for the two substrates are significantly different and at least one is quite large and reactions are run to high conversions.[18]

According to Hormiats and Van Artsdalen, the gas-phase bromination of neopentane gives $n = 1.2$ at 107 °C, but the value decreases somewhat with decreasing temperature.[19] Methylene chloride has not been investigated, but n for $CHCl_3$ involving a structurally similar radical is 0.04 and temperature invariant.[20] Our isotope tracer experiment implies that n for CH_2Cl_2 is ≤0.25. These small n values all say that reversibility should, at most, lead to small *decreases* in measured r's at high conversions and are consistent with the bulk of the experiments described above.

Reactions of N-Iodosuccinimide (NIS). A strong argument for the S_σ·–S_π· scheme has been based upon the reported behavior of NIS, stated to give a high yield of β-iodopropionyl isocyanate

(15) Walling, C.; Helmreich, W. *J. Am. Chem. Soc.* **1959**, *81*, 1144.
(16) (a) Tanner, D. D.; Pace, T.; Ochiai, T. *Can. J. Chem.* **1975**, *53*, 2202. (b) Tanner, D. D.; Kosugi, Y.; Archart, R.; Wada, N.; Pace, J.; Ruo, T. *J. Am. Chem. Soc.* **1976**, *98*, 6275. (c) Tanner, D. D.; Pace, T.; Ochiai, T. *J. Am. Chem. Soc.* **1975**, *97*, 4303.
(17) Zavitsas, A. A.; Fogel, G.; Halwagi, K. E.; Legotte, P. A. D. *J. Am. Chem. Soc.* **1983**, *105*, 6960. These authors have used an integrated form of the original differential equation.
(18) Calculation using essentially Zavitsas' integrated equation[17] shows that for two substrates A and B with $n_A = 1.0$, $n_B = 0.0$ measured r's (A/B) will be 74% and 44% of their true value at 58% and 100% reaction of Br_2.
(19) Hormats, E. I.; Van Artsdalen, E. R. *J. Chem. Phys.* **1951**, *19*, 778.
(20) Sullivan, J. H.; Davidson, N. *J. Chem. Phys.* **1951**, *19*, 143. The n values for 1-bromo- and 1-chloro-1-butyl radicals are also small.[16]
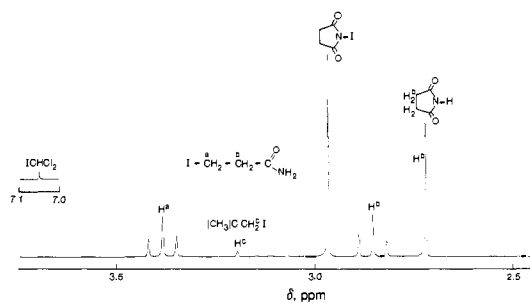

Figure 5. ^1H NMR spectrum (200 MHz) of the reaction product mixture from the photoiodination of neopentane and methylene chloride with NIS–I_2.

and a large r value in the presence of allene as a halogen atom trap, but no isocyanate and $r = 1.1$ in the presence of I_2.[7a] However, since the yield of alkyl iodides in the latter experiment was under 3%, it seemed unconvincing and we have examined the NIS–I_2 system ourselves. Table IV shows results of five experiments. Although our r's are close to Skell's, our analytical method indicates that ~75% of the product is actually isocyanate and that yields of alkyl iodides are low, accounting for less than half of the 25% succinimide formed. Figure 5 shows the NMR of a typical reaction after hydrolysis of the isocayanate to β-iodopropionamide. Although schemes might be devised to make this result consistent with the S_σ·–S_π· hypothesis, the argument obviously loses much of its force. Since iodine atoms alone do not react with the substrates under these conditions, some other chain carrier would seem to be involved, possibly an NIS–I· complex of the sort previously suggested for NBS–Br· systems.[3] On the other hand, from our parameters, the number of succinimide radicals required to produce the observed isocyanate should themselves have produced at least as much of the two alkyl iodides as we find, so there is hardly room for another chain unless alkyl iodides are being destroyed as well as formed. We can only conclude that NIS experiments, at this point, give complex results and tell us nothing significant about "X·" in NBS reactions.

Discussion

As we have seen, in competitive brominations of neopentane–CH_2Cl_2 application of our new analytical methods to NBS–olefin systems and reexamination of reactions of Br_2 alone yield data in substantial agreement with previous results. However, with NBS alone or particularly with NBS–Br_2 (Skell's "S_π·" conditions) there is substantial disagreement since we find variable r's and significant yields of BPI. We believe the discrepancies arise because of the insensitivity of former analytical methods and their failure to allow for inadvertent hydrolysis of BPI. We should also point out that the actual documentation of $S·_\pi$ behavior ($r \simeq 1$, no BPI) in NBS–Br_2 reactions for this substrate pair is scanty. In their original communication[5a] the Skell group reported without details that six experiments gave this result, but, as shown in this paper, neither at Utah nor Alberta have we been able to confirm this result under the conditions of the single experiment later reported in detail,[11] and we feel that the earlier failure to detect BPI in NBS–Br_2 reactions at Utah[3] was due to insensitivity of the 60-MHz NMR analyses.

Our basic conclusion is that, under most conditions, mixed chains are involved and that most experiments are consistent with S· and Br· as the chain carriers. However, a few experiments seem to require some third-chain carrier with an intermediate r value which does not yield BPI. Most puzzling in this regard are the

experiments at the end of Table III intended to reproduce the Skell experiment mentioned above,[11] which were run at NBS concentrations above its solubility so that the systems were heterogeneous. Although some approach Skell's report of $r = 1$ and no BPI, BPI was always found, at least in small quantities. What is surprising is that both r and Y *increase* with conversion. Since Br_2/NBS ratios are increasing this would not be expected for competing S_σ·–S_π· chains, for S·–Br· chains, or for any combination of the two. This oddity may arise because we are dealing with a heterogenous system. However, these conditions also produce a solution saturated with succinimide, and we have previously reported[3] that r_{Br} for Br_2 in this system increases to ~0.4 in the presence of succinimide. While the significance of this observation has been questioned by Skell,[7d] it may indeed be true that we are seeing a perterbation of Br· selectivity through some sort of complexing, and we do not see these results as compelling evidence for the S_π·–S_σ· scheme.

To round matters out we will now discuss the status of results on other systems whch have been examined, attempting to distinguish between data which should discriminate between the S_σ·–S_π· and S·–Br· hypotheses and those which are simply consistent with either.

An important argument for S_σ·–S_π· has been the iodination of neopentane–CH_2Cl_2 mixtures by NIS–I_2, reported[7a] to give no iodoisocyanate (IPI). By our methods we find some 75% IPI, and the following paper[2] reports similar IPI yields for the NIS–I_2 reaction in $CHCl_3$, so we consider this argument invalid.

Skell has reported that as reactive substrates giving rise to tertiary or allylic radicals are added to NBS–CH_2Cl_2–olefin systems, the $CHCl_2Br$/BPI ratio in the products increases, indicating CH_2Cl_2 bromination by another, non-BPI-producing radical identified as S_π·.[7b]

The following paper[21] fails to confirm this increase and shows that 2,3-dimethylbutane, cyclohexene, and butadiene in this reaction give major yields of polybrominated products, consistent with substantial participation of Br· chains.

A 1983 paper from Alberta[4] proposed that data on the competitive bromination of cyclohexane–cyclopentane were entirely consistent with competing S·–Br· chains (although the results could not be analyzed in the detail we have used here to clearly exclude two S· states). This conclusion was criticized by Skell,[7e] but, as we have shown elsewhere,[22] his two crucial experiments (reporting no BPI in the presence of CCl_3Br or benzene, see below) were carried to such low conversion that the amount of BPI predicted from the reported r values and the S·–Br· hypothesis could not have been detected by his analytical method.

An important tenet of the S_σ–S_π hypothesis has been that CCl_3· reacts with NBS to yield S_π·, a conclusion based on the failure to observe BPI in the NBS bromination of $CHCl_3$ in the presence of vinylidene chloride[7b] or in NBS brominations in CH_2Cl_2 in the presence of olefin and high concentrations of CCl_3Br.[7c] The chloroform result could not be confirmed at Utah[3] or Alberta,[21] and high yields of BPI were obtained, and have been observed in experiments using *tert*-butylethylene[7b] or allyl chloride[23] (the system with which BPI was originally detected).[24]

The effect of CCl_3Br has not been reexamined in as much detail, but we have shown elsewhere[22] that, in competitive bromination of cyclohexane–cyclopentane in CH_2Cl_2, 2 M CCl_3Br reduces rather than eliminates BPI. Further, CCl_4 (a much poorer CCl_3· source) produces the same effect, and we attribute both to the resulting reduced solubility of NBS favoring Br· chains (and also any reversibility[7a] of ring opening).

Finally, Skell has shown convincingly that S· adds to benzene to yield (eventually) *N*-phenylsuccinimide[2] and has proposed that

the intermediate cyclohexadienyl radical reacts with NBS to yield S_π·.[7b] In the following paper[21] we show that in the presence of olefin even 2.5 M benzene (again a poor solvent for NBS) reduces rather than eliminates BPI. Further the reaction is messy and is evidently a copious source of Br_2 (or some species equivalent to it) since both olefin dibromide and other polybrominated compounds are major products. We see nothing in these data inconsistent with competing S· and Br· chains with benzene acting as a trap for S· and olefin and cyclohexadienyl intermediates trapping Br· and Br_2·. We believe that all reliable experimental results involving product distributions are now consistent with S·–Br· chains, and some (as those presented in this paper) are inconsistent with the S_σ·–S_π· scheme as presently formulated.

Some comments are also in order on the kinetics of these brominations and on kinetics of competitive chains in general. Aside from Dauben's early results,[25] the only kinetic study of NBS brominations has been the preliminary report from Utah[3] which indicated that the rate constants for hydrogen abstraction by S· and the chain carrier in NBS–Br_2 systems (whatever it is) were both rather small. Although these results have been criticized,[7c] the fact remains that overall rates of NBS brominations of aliphatic substrates are relatively slow—complete reaction usually requiring several hours under strong UV irradiation (conditions which give almost explosive reactions with Cl_2 or *tert*-butyl hypochlorite), and kinetic chains, whether estimated from quantum yields,[7a] rates of initiator decomposition,[3] or yields of Br_2 addition products to olefinic Br· traps (this paper), rarely over 10^3.

Some data in a 1972 paper by Davies, Roberts, and Smith,[26] which has so far been overlooked in this controversy, also bears on the slowness of S· reactions. These investigators showed that the reaction of NBS with tetraalkylstannanes was a radical chain process with propagating steps (S = the succinimide radical).

$$S· + R_4Sn \rightarrow S\text{-}SnR_3 + R· \qquad (8)$$

$$R· + NBS \rightarrow RBr + S· \qquad (9)$$
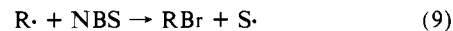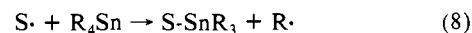
For a variety of R's k_8 was estimated as 4×10^3–3×10^4, and since the reactions occur in an almost quantitative yield as indicated, this clearly puts an upper limit on the rate constant for ring-opening of the S· radical. Further, the rate constant with R· = benzyl was somewhat larger than that for R· = 1° alkyl, which seems inconsistent with the S_σ·–S_π· hypothesis, since in (9) R· = benzyl should have generated S_π· and R· = 1° alkyl the more reactive S_σ·.

Rates of NBS–olefin and NBS–Br_2 reactions are roughly similar,[27] and both are faster (by a factor of 10–100) than reactions of Br_2 alone, at least with substrates such as CH_2Cl_2 and neopentane. At first glance, these qualitative observations may seem difficult to reconcile with competing S· and Br· chains, since a reaction going chiefly through a Br· chain should show a rate close to that with Br_2 alone. Two observations, however, may remove the difficulty. First, by analogy to the behavior of amidyl radicals, the rate constant for bimolecular termination of succinimidyl radicals is probably 10^9 s⁻¹ or smaller,[3] while the value for Br· is 2×10^{10} s⁻¹.[28] Any replacement of Br· by S· should lead to longer radical lifetimes. The second involves the role of HBr in Br_2 reactions. In principle, reversibility could lead to reduced rates, but we have concluded above that reversibility is unimportant in neopentane–CH_2Cl_2 systems except at high conversions. On the other hand, Skell has reported in some detail[7d] that adding K_2CO_3 as an HBr trap increases the rate of neopentane–CH_2Cl_2 brominations by a factor of 5–10. Since NBS also removes HBr, this could account for much of the difference in rate between NBS and Br_2 reactions, but if we are correct about reversibility it implies

(21) Tanner, D. D.; Meintzer, C. P. *J. Am. Chem. Soc.*, following paper in this issue.

(22) Tanner, D. D.; Meintzer, C. P.; Tan, S. L. *J. Org. Chem.* **1985**, *50*, 1534.

(23) Johnson, H. W.; Bublitz, D. E. *J. Am. Chem. Soc.* **1958**, *80*, 3150.

(24) Skell's ingeneous explanation[7b] of this difference was that CCl_3· adds to *tert*-butylethylene or allyl chloride to yield a 2° radical which in turn converts NBS to S_π·, but that CCl_3· does not add to vinylidene chloride.

(25) Dauben, H. J. Jr.; McCoy, L. L. *J. Am. Chem. Soc.* **1959**, *81*, 4863.

(26) Davies, A. G.; Roberts, B. P.; Smith, J. M. *J. Chem. Soc., Perkin Trans. 2* **1972**, 2221.

(27) There are conflicting results as to which is faster under similar conditions, but few if any comparions have been made with known, identical rates of chain initiation.

(28) Strong, R. L. *J. Am. Chem. Soc.* **1965**, *87*, 3563. This result is in CCl_4, and the rate may be higher in more fluid CH_2Cl_2.
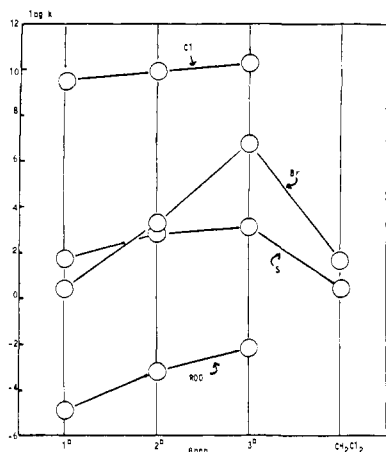
Figure 6. Rate constants for radical attack on C–H Bonds (ROO. = *t*-BuOO).

some deactivation of Br·, e.g., by complexing with HBr to give unreactive HBr₂·.[29]

At present, therefore, we do not think that these rate differences provide a convincing argument against competing S· and Br· chains. Accordingly, we feel that the rate constants deduced from our kinetic study of the NBS–Br₂ system[3] involve both Br· and S·. In fact, since we conclude that such reactions are going chiefly through Br· chains, they are probably close to Br· rate constants (see below).

In such systems, a rapid equilibration

$$S· + Br_2 \rightleftharpoons NBS + Br· \qquad (10)$$
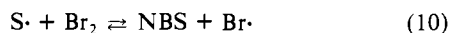
is generally accepted. Skell has assumed the exchange to be thermoneutral with an equilibrium constant of unity, citing a paper by Howard and Skinner,[30] who determined the difference in S–H and S–Br bonds in succinimide and NBS as $D(S-H) - D(S-B) = 57.35 + \Delta_2$ kcal/mol where Δ_2 is the difference in heats of sublimation of NBS and succinimide and, assuming that $D(S-H)$ was probably 100 kcal or less, concluded that $D(S-Br)$ was "not very different" from that in Br₂. Actually, taking Δ_2 as −2 kcal/mol[31] and $D(Br-Br) = 46.1$ kcal/mol gives $D(S-H) = 102$ kcal. While the result is plausible it is highly conjectural, since there is no direct measurement of $D(S-H)$ for succinimide or any other amide or imide. Accordingly, the equilibrium constant in (10) could easily differ from unity by several powers of 10, and an argument for a lower value is given below.

To examine further the expected properties of competing chains, Figure 6 summarizes what is known about actual rate constants for reaction of several radicals with 1°, 2°, and 3° C–H bonds and with CH₂Cl₂. Halogen atom[32] and peroxy radical[33] values are taken from the literature (the former come from gas phase data), and the point for Br· + CH₂Cl₂ is calculated from the 1° C–H value and our $r_{Br} = 0.056$. Numbers for S· reactions are from the kinetic study cited[3] and r values from this and the following papers. As indicated, the S· + 3° C–H point is a maximum value, since even in the presence of vinylidene chloride some of the reaction appears to go through the Br· chain.[21]

Before comparing the S· and Br· data, we note two interesting facts. First, $k = 20$ for the Br· + CH₂Cl₂ reaction (per H) is in remarkably good agreement with the value of $k = 55$ (per molecule at 50°) from our kinetic study of the NBS–Br₂ system,[3] supporting

our present contention that the reaction is chiefly a Br· chain. Second, there are two pairs of radicals which show similar selectivities and energetics but widely different rates: Br· and RO₂·, and Cl· and S·.[34]

When we compare S· and Br· reactions, it is clear that, if our S· values are anywhere near correct, the curves cross with Br· reactions significantly faster for weak C–H bonds. Further, the data suggest that the equilibrium constant for S· ⇌ Br· interchange, (8), must actually be considerably larger than unity. Taking our estimate of the rate of ring opening of S· as 1.5×10^4 in 15 M CH₂Cl₂, the ratio of CHCl₂Br formed via Br· reactions to BPI, $[CHCl_2Br]_{Br}/[BPI] = 20 \times 2 \times 15[Br_2]K/1.5 \times 10^4-[NBS]$. From the data of Table III, at 100:1 [NBS]/[Br₂] this ratio is at least unity, requiring $K \geqslant 250$. If K has such a large value, with more reactive substrates mere traces of Br₂ should swamp out S· chains, consistent with our conclusion that tertiary and allylic substrates are consumed by Br· chains even in the presence of added olefinic Br· traps.[35] With *N*-chlorosuccinimide the competition between S· and Cl· chains should be even less favorable, since, while K should be a little smaller, Cl· k's are very much larger, and it would be surprising if S· chains could be observed at all. Although Skell has given another interpretation,[7a] this seems the simplest explanation of the failure to observe either ring opening or S· addition to aromatics in *N*-chlorosuccinimide reactions.

Conversely, in sufficiently unreactive media, S· reactions should predominate even in the presence of Br₂. We now believe that this rather than any postulated ring-opening of a photoexcited NBS molecule is the explanation of the high yields of BPI observed in some brominations by NBS–Br₂ of CD₂Cl₂ alone[3] (and also that all attempts to measure kinetic isotope effects in these systems[3,7c] are probably confounded by competing chains).

In summary, we believe that the "Sₒ·" species is simply a ground-state S· radical, the properties of which are now quite well defined. All attempts to demonstrate a second "Sₓ·" state with properties clearly associated with a succinimide radical have been unsuccessful and the Sₒ·–Sₓ· hypothesis is at best unnecessary. Although some experiments still imply incursion of a X· species with a selectivity different from Br·, the bulk of the data, both on products and kinetics, are entirely consistent simply with competing S· and Br· chains.

Experimental Section

Materials. Neopentane (Phillips 66, research grade, >99.9%) was distilled prior to use.[36]

Bromine (Fisher Scientific) was washed twice with concentrated sulfuric acid, decanted, and fractionally distilled (18-in. Vigreux column) from P₂O₅. The middle fraction was collected.

N-**Bromosuccinimide** (Fisher Scientific Co.) was recrystallized from hot water and dried over P₂O₅ in vacuo for 48 h. Titration showed it to be more than 99.55% pure. It was sealed and stored at 0 °C in the dark. The container was warmed to room temperature before opening.

N-**Iodosuccinimide** (Arapahoe Chemicals) was recrystallized from hot acetone and shown by titration to be more than 99.2% pure.

Iodine (Terochem Laboratories) was sublimed before use.

Ethylene (Matheson, research grade >99.98%) was distilled before use.

Methylene chloride (Caledon Chemical Co.) was dried over calcium chloride and distilled with use of a 1-m Teflon spinning-band column. GLC analysis showed it to be 99.98% pure. Traces of chloroform were detected.

(29) In water Br· reacts with Br⁻ to give relatively unreactive Br₂⁻· (the conjugate base of HBr₂·).

(30) Howard, P. B.; Skinner, H. A. *J. Chem. Soc. A* **1966**, 1536.

(31) From standard tables, the heats of vaporization of succinimide and succinic anhydride are 16.4 and 14.7 kcal/mol, the difference probably being due to H-bonding. Since the anhydride and NBS have similar properties and shapes, we assume a similar difference.

(32) Kerr, J. A. In "Free Radicals"; Kochi, J. K., Ed.; John Wiley and Sons: New York 1973; Vol. I, p 15 (Table III).

(33) Ingold, K. U. In "Free Radicals"; Kochi, J. K., Ed.; John Wiley and Sons: New York 1973; Vol. I, p 74 (Table VI).

(34) The Br·–RO₂· comparison has long been available (if not generally recognized) and is a notable exception of the "similar selectivity–similar rate" assumption.

(35) In justice, this whole picture of competing S·–Br· chains was given qualitatively by Skell 10 years ago (before the Sₒ·–Sₓ· hypothesis appeared) in explaining why allylic brominations are best carried out in poor solvents for NBS. Day, J. C.; Lindstrom, M. J.; Skell, P. S. *J. Am. Chem. Soc.* **1974**, *96*, 5616.

(36) Phillips Petroleum Co., Bulletin 526. The neopentane obtained was produced from the fractional distillation of a light petroleum fraction. The fraction with the highest purity was marketed as research grade >99.9% and contained traces of *n*-butane. A less pure fraction >99.6% was marketed as pure grade and contained *n*-butane and *cis*-butene-2 as identified impurities. One neopentane sample, used in early work, contained significant olefin and gave erratic results (not included in tables).

Vinylidene chloride (Aldrich Chemical) was distilled under nitrogen immediately prior to use.

β-Bromopropionamide was prepared from β-bromopropionic acid by heating to reflux with PCl_3, followed by addition of ammonium hydroxide.[37] The precipitated product was washed three times with ice-cold water and dried: mp 110–113 °C (lit.[38] mp 111 °C); 80-MHz ^{1}H NMR data δ 2.75 (t, J = 7 Hz, 2 H), 3.61 (t, J = 7 Hz, 2 H), 6.20 (br s, 2 H).

β-Iodopropionamide was prepared from β-iodopropionic acid by heating to reflux with PCl_3, followed by addition of ammonium hydroxide.[36] The precipitated product was dried by suction and recrystallized from acetonitrile: mp 135–136 °C dec (lit.[39] mp 140.5 °C); 80-MHz ^{1}H NMR data δ 2.86 (t, J = 6.9 Hz, 2 H), 3.37 (t, J = 6.9 Hz, 2 H), 5.66 (br s, 2 H), MS; m/e 199 (29.1), 127 (12.9), 72 (98.2), 55 (7.8), 44 (100), 28 (16.4).

Neopentyl iodide was prepared from neopentane and *tert*-butyl hypoiodite.[40] The colorless liquid product was kept in the dark, as it rapidly turned the color characteristic of iodine upon exposure to light: bp 39–41 °C at 30 mm (lit.[41] bp, 47–50 °C at 40–45 mm); 80-MHz ^{1}H NMR data δ 1.07 (s, 9 H), 3.19 (s, 2 H).

Iododichloromethane was prepared from chloroform, methyl iodide, and $AlCl_3$ following the procedure of Seyferth and Haas.[42] The colorless liquid product was kept in the dark, as it rapidly turned the color characteristic of iodine upon exposure to light: bp 120–126 °C at 710 mm (lit.[17] bp 132 °C at 760 mm); 80-MHz ^{1}H NMR data δ 7.10 (s).

The Photobromination of Methylene Chloride and Neopentane with NBS. Mixtures of NBS, methylene chloride, and manometrically measured amounts of neopentane were placed in Pyrex reaction ampules in the absence of light. The ampules were degassed, sealed, and thermostated at 15 °C. After equilibration the reaction vessels were irradiated in a Pyrex thermostat by using a 400 W General Electric sunlamp. When additives, ethylene, vinylidene chloride, or molecular bromine, were included, they were added either as manometrically measured amounts (ethylene) as liquid (vinylidene chloride) or as aliquots of standard methylene chloride solutions (molecular bromine).

After irradiation, the reaction tubes were frozen, opened, and analyzed by one of the following methods: (A) Brominated products were determined by GLC analysis of an aliquot to which C_2Cl_6 had been added as an internal standard (50-m methyl silicone capillary column (30–100 °C)). The percentage reaction was determined by iodometric titration with aqueous thiosulfate. The aqueous solution was separated from the organic layer. The water was distilled under reduced pressure, a standard was added to the residue, and the material which was soluble in acetonitrile was analyzed for succinimide and BPA on a 50-m methyl silicone capillary column (150–170 °C) with butyramide, valeramide, or hexanamide as internal standards. Control experiments on standard mixtures of products substantiated the validity of the analytical procedure. For reactions which had run to completion, the two GLC analyses were carried out directly on aliquots of the reaction mixture. (B) The GLC analysis for succinimide and BPA above was replaced by ^{1}H FT NMR analysis at 200 MHz in CD_2Cl_2 (Bruckner instrument, 40 scans). (C) Reaction mixtures were analyzed directly by FT NMR as above, after adding a trace of water to convert BPI to BPA and enough CD_2Cl_2 and CH_2Cl_2 to give a homogeneous solution if necessary. The $CHCl_2Br/$ $C_5H_{11}Br$ ratio was also determined by GLC as above, since this provides a more accurate ratio when yields are low.

Experiments at Utah were carried out similarly, except that reaction mixtures were flushed with argon, and irradiation was at 20 °C with a 450 W medium-pressure Hanovia Hg lamp. Analysis (after adding H_2O) was by 300-MHz ^{1}H NMR (Varian SC 300 instrument) with CD_2Cl_2 lock and simultaneous CH_2Cl_2 homonuclear decoupling. Spectra were very similar to Figures 1 and 2 with both BPI and BPA clearly detectable before hydrolysis. One Utah run was analyzed by both laboratories and gave results in agreement within the accuracy of the NMR integrations (±2%).

Vapor-Phase Bromination of Neopentane and Methylene Chloride. Mixtures of neopentane and methylene chloride were manometrically measured and transferred in vacuo to a reaction vessel equipped with a break seal. Molecular bromine was weighted into a separate break seal attached to a vacuum line and degassed. The two break seals were attached to the reaction vessel (12- or 0.5-L bulbs), and the break seals were opened in the absence of light in the order neopentane/dichloromethane and bromine, with 15 min intervals between. The gaseous

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Table V. Photobromination of CH_2Cl_2–Neopentane by Br_2

[Br_2]	[CH_2Cl_2]	[C_5H_{12}]⁻	% of reaction	
2.34 × 10⁻⁴ ᵃ	4.5 × 10⁻⁵	4.2 × 10⁻⁵	0.5	0.038
2.35 × 10⁻⁴ ᵃ	4.6 × 10⁻⁵	4.8 × 10⁻⁵	0.5	0.038
2.75 × 10⁻³ ᵃ	4.5 × 10⁻³	4.5 × 10⁻³	1.0	0.035
0.542	12.33	1.79	8.15	0.047 ± 0.004 (3)
0.098	11.4	2.30	12.2	0.067
0.49	11.4	2.30	3.7	0.055
0.98	11.23	2.39	2.6	0.11
0.42	11.13	2.45	5.5	0.12
8.0	7.08	1.18	0.014–0.11	0.10 ± 0.02 (4)

ᵃ Gas-phase reactions. ᵇ Experimental errors are standard deviations of the indicated number of runs.

mixture was allowed to equilibrate for 1 h at 23 or 15 °C, and the vessel was irradiated with incandescent light (300 W). The contents of the bulbs were condensed with liquid nitrogen into a tube attached to the reaction vessel, and the sample was removed from the vacuum line. A methylene chloride solution of a standard, hexachloroethane, was added, and the excess bromine and hydrogen bromide were destroyed with cold (0 °C) sodium bisulfite. The organic layer was analyzed by GLC (50-m methyl silicone capillary column). Results appear in Table V.

A mixture of the reactants, with added amounts of a synthetic mixture of the products of bromination, was subjected to the reaction conditions, isolation and analytical conditions, except that the mixture was never exposed to irradiation. The ratio of products, bromodichloromethane/ neopentyl bromide, was the same (±2.3%) as the original ratio of added products.

Liquid-phase brominations of neopentane and methylene chloride with Br_2 were carried out in the same manner as the NBS reactions. After the reaction, the reaction tubes were frozen and the frozen mixtures were treated with a concentrated aqueous solution of sodium bisulfite to destroy the excess bromine. An aliquot sample of a methylene chloride solution of a standard, hexachloroethane, was added and the mixture was quantitatively analyzed by GLC (50-m methyl silicone capillary column). Results are shown in Table V.

Mixtures of reactants also containing synthetic mixtures of products were subjected to the reaction conditions, and isolation, and analytical procedures, but in the absence of light. A comparison of the relative ratios of products, from an analysis of the product mixtures before and after this procedure, showed them to be the same (±2%). A preanalyzed methylene chloride solution of the bromination products, bromodichloromethane and neopentyl bromide, were thermostated (15 °C) and irradiated by using the same apparatus as was used for the other liquid-phase brominations of neopentane and methylene chloride. After a period of irradiation approximately twice as long as the other brominations, the reisolated products were reanalyzed and found to be the same (±4%) as the preanalyzed product mixture.

Bromination of CD_2Cl_2 **and Neopentane in** CCl_4 **with** Br_2 **and HBr.** A CCl_4 solution containing CD_2Cl_2 (1 M) and molecular bromine (0.24 M) was placed in a Pyrex ampule. Neopentane and HBr were added manometrically: [neopentane] = 0.17 M, [HBr] = 0.25 M. The mixture was degassed, sealed, equilibrated at 15 °C, and irradiated.

The mixture was titrated iodometrically and found to have undergone 24.5% reaction. The remaining methylene chloride was collected by GLC (6-ft × ^{1}/₈-in. stainless steel column, *n*-octane/Porasil C, 100–120 mesh, 10 cm³/min, 70 °C), and samples of the original (before reaction) and recovered materials were submitted to mass spectral analysis. On the basis of the original and final ratios of M^+/e = 89, 1.0 mol % of protium was found to have been incorporated into the unreacted dichloromethane (approximately equal to one hydrogen reversal reaction for every four brominated products formed).

The Photolodination of Methylene Chloride and Neopentane with NIS and Iodine in the Solvent Methylene Chloride. Mixtures of NIS, I_2, methylene chloride, and manometrically measured amounts of neopentane were placed in Pyrex reaction ampules in the absence of light. The ampules were degassed, sealed, and thermostated at 15 °C. After equilibration the reaction vessels were irradiated in the same apparatus used for the NBS reactions. After irradiation (~3 h), the reaction tubes were frozen and then opened and a calculated amount of water was added (just sufficient to react with the IPI). An aliquot sample was sealed in an NMR tube and analyzed for products by 200-MHz ^{1}H NMR spectroscopy.

The remaining solution was titrated iodometrically with aqueous sodium thiosulfate. The organic mixture was analyzed by GLC (50-m

methyl silicone capillary column), and the products were measured relative to an internal standard, hexachloroethane.

The yields of β-IPI and succinimide were determined from the NMR spectrum, and the neopentyl iodide and iododichloromethane were determined from the GLC traces.

Appendix

Derivation of (6): assuming reactions 1–5 given earlier, to obtain r

$$\frac{-d[A]/dt}{-d[B]/dt} = \frac{k_1[A][S\cdot] + k_2[A][X\cdot]}{k_3[B][S\cdot] + k_4[B][X\cdot]} \quad (11)$$

If [A] and [B] do not change significantly during reaction and r' is the relative reactivity A/B per molecule (=6r) we may integrate

$$\frac{\Delta[A]/[A]}{\Delta[B]/[B]} = r' = \frac{k_1 + k_2 \int [X\cdot]\, dt / \int [S\cdot]\, dt}{k_3 + k_4 \int [X\cdot]\, dt / \int [S\cdot]\, dt} \quad (12)$$

Similarly, to obtain the yield of BPI, Y

$$\frac{d[BPI]/dt}{d[total\ products]/dt} = $$

$$\frac{k_5[S\cdot]}{(k_1[A] + k_3[B] + k_5)[S\cdot] + (k_2[A] + k_4[B])[X\cdot]} \quad (13)$$

Integrating

$$\frac{1}{Y} = \frac{k_1[A] + k_3[B] + k_5}{k_5} + \frac{k_2[A] + k_4[B]}{k_5}\frac{\int [X\cdot]\, dt}{\int [S\cdot]\, dt} \quad (14)$$

Noting that $(k_1[A] + k_3[B] + k_5)/k_5 = 1/Y_s$, where Y_s is the BPI yield expected for a pure S· chain, the ratio of integrals may be eliminated between (12) and (14) to yield (after some algebra) (6). Since the integrals vanish, the relation between r and Y is independent of how [Br·] and [S·] vary with reaction.

To extend this treatment to a series of X_i's, $k_2[X\cdot]$ and $k_4[X\cdot]$ must be replaced by $\sum k_{2i}[X_i]$ and $\sum k_4[X_i]$. If this is done k_2/k_4 in (6) will be replaced by $\sum k_{2i}\int [X_i\cdot]\, dt / \sum k_{4i}\int [X_i\cdot]\, dt$, which we term the "effective k_2/k_4" since it determines the ratio of products produced from A and B by all radicals except S·.

Reexamination of the Reaction of a "Graded Set" of Radicals with N-Bromosuccinimide:[1] A Kinetic Argument Concerning the π and σ States of Succinimidyl

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Abstract: The NBS brominations of methylene chloride with added substrates which yield stable radicals were reinvestigated. The proposal that these substrates would affect the ratio of β-bromopropionyl isocyanate (BPI)/bromodichloromethane, the solvent bromination product, was not substantiated. Bromination of 2,3-dimethylbutane, cyclohexene, and butadiene by NBS in CH$_2$Cl$_2$ plus vinylidene chloride gives essentially the same BPI/CHCl$_2$Br ratios as in the presence of neopentane but large yields of brominated and polybrominated products. Similar reactions in the presence of up to 2.5 M benzene always yield BPI but also highly brominated benzene derivatives. BPI is detected in the NBS bromination of chloroform under all conditions and is the major product in the presence of vinylidene chloride. Photolysis of N-iodosuccinimide–I$_2$ in CHCl$_3$ gives β-iodopropionyl isocyanate as the chief product. None of these observations support the hypothesis of σ and π states of the succinimidyl radical, while the NBS results appear consistent with competing S·–Br· chains.

In a series of papers starting in 1978[3] Skell has proposed that radical chain brominations by N-bromosuccinimide (NBS) may proceed through two different succinimidyl radicals, an excited S$_\sigma$· generated by the exothermic reaction of reactive primary and seconary radicals with NBS, and a ground-state S$_\pi$· from the reaction of allylic radicals, CCl$_3$· and Br· with NBS (tertiary

radicals were proposed to give both S$_\sigma$· and S$_\pi$·). These S$_\sigma$· and S$_\pi$· radicals show different selectivities (r's) for pairs of substrates, and only S$_\sigma$· undergoes ring opening to yield β-bromopropionyl isocyanate (BPI). The strongest evidence for Skell's proposal has come from his data on product distributions in the NBS–CH$_2$Cl$_2$–neopentane system. However, in the preceding paper,[4] we have shown that, when the products formed in this system are reexamined by what we believe to be a more reliable analytical method (high-field NMR, supplemented by GC analysis), most of the results are consistent with simple competing succinimidyl radical (S·, equivalent in properties to Skell's S$_\sigma$·) and bromine atoms as the chain carrying species. The mixed chain, S· and Br·, has been shown previously to control the reactions of the more reactive substrates cyclohexane and cyclopentane.[5]

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