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Photodecomposition of *N*-Bromosuccinimide: Radical Chain Carriers and Their Interrelations

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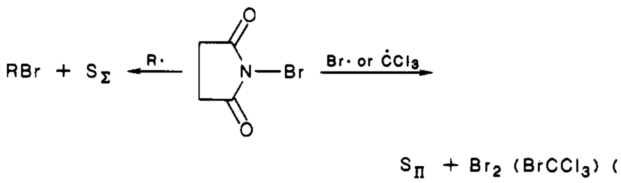
The direct photolysis of *N*-bromosuccinimide (NBS) in the absence and presence of bromine and its bromine atom initiated decomposition were investigated by selective irradiation of NBS or Br_2 and by critically examining the β-bromopropionyl isocyanate (BPI) yields and the relative selectivity of intermolecular H abstraction from cyclohexane and CH_2Cl_2. Experimental results showed (i) that direct photolysis of NBS gave extra amounts of BPI, (ii) that the bromine atom initiated NBS decomposition also generated BPI, and (iii) that the interaction of bromine atoms with NBS or the succinimidyl radical with bromine set up a rapid equilibrium of the radicals. In the NBS + Br_2 system the relative selectivities of intermolecular H abstraction, $k_{C_6H_{12}}/k_{CH_2Cl_2}$, were 16–22, practically the same as those for a bromine atom (15–18), and the BPI percent yields decreased systematically as both initial and observed bromine concentrations increased in the range of 1–100 mM. Therefore, the photodecomposition of the NBS + Br_2 system involves the succinimidyl radical and bromine atom in a fast equilibrium and as the radical-propagating species, without the need to invoke another radical. The succinimidyl radical generated from direct photolysis of NBS is proposed to be a vibrationally excited hot species that undergoes much faster ring opening than the ground-state species. These results provide a satisfactory explanation to resolve the most recent controversy over the number of radical intermediates involved in the NBS photodecomposition.

The controversy over the nature of the chain-propagating species in the photodecomposition of *N*-bromosuccinimide (NBS) has been widely recognized in recent conferences[2] and documented in reviews[3,4] and research reports[5-11] and continues to attract attention in recent publications.[12-14] The areas of disagreement involve both experimental results and their interpretations. Skell's group has claimed[4-9] that two radical chain carriers, in addition to Br·, are involved in propagation steps in the decomposition of NBS under a wide variety of conditions, either in the presence of bromine or that of olefins (Br· and bromine scavengers).[4,9,15,16] These two chain carriers were claimed to be generated in the propagation step[5,6] (eq 1) and were postulated to be the ground-state Π radical (S_Π) and the excited-state Σ radical (S_Σ). In the most recent paper,[14] Skell's group has withdrawn the Σ–Π postulation but reiterates the presence of two radical chain carriers in addition to Br·.



(1)

Tanner and co-workers[11-13] have interpreted their results as a mixed chain reaction of a single succinimidyl radical and Br·. Walling et al. initially[10] recognized the involvement of two radical intermediates along with Br· but recently[13] arrived at the same conclusion as Tanner. The divergence no doubt arises from the complexity of the photodecomposition, which involves multiplicity of chain carriers, bromine transfer agents, and initiation species, leading to considerable discrepancy in experimental data. Working on different imidyl models,[17] we have arrived at the conclusion that photodecomposition of *N*-bromoimide generally involves the imidyl, Br·, and bromine radical complex (BRC) as the chain carriers in propagating radical addition or abstraction reactions and that the single imidyl radical identified should possess a Σ electronic configuration.

The source of these disagreements is centered around the NBS photodecomposition without the addition of an olefin scavenger and in the presence of bromine (what Skell called "the S_Π conditions").[6,8,13] Using neopentane and CH_2Cl_2 as competing substrates for intermolecular H abstraction, Skell's group obtained, under these limiting conditions, a constant relative selectivity, $k_{(CH_3)_4C}/k_{CH_2Cl_2}$ (per hydrogen), for a third radical of 1.0 and a lack of β-bromopropionyl isocyanate (BPI) formation. Unfortunately, the relative reactivity of 1.0 is a figure between those of S_Σ and Br·, 17 and 0.07, respectively, and poses some ambiguity to the existence of a third radical. Since the formation of BPI was used by Skell's group as a criterion to judge the "S_Σ or S_Π chain carrier" in the thermal propagation processes,[7] its absence in the photodecomposition has been a controversial issue between the two sides.[5-16] It will be shown here that the photolytically generated succinimidyl radical undergoes ring opening even more efficiently than a thermally generated one does to give an extraneous source of BPI. Thus, the reported differences in BPI yields among these groups[5-16] are largely artifacts of experimental design.

In our previous work, we found that NBS decomposition is a complex reaction and not amenable to quantitative

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[2] For example: (a) 4th International Symposium on Organic Free Radicals, University of St. Andrews, July 9–14, 1984. (b) International Chemical Congress of Pacific Basin Societies, Symposium on Free Radicals and Electron Transfer Reactions, Honolulu, HI, Dec 1984.

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Table I. BPI Percent Yields from the Photolysis of NBS[a]

expt	solvent	additive (mM)	BPI, mM	SH, mM	t, min	BPI, %
		A. Irradiation through a Pyrex Filter				
1	CH_2Cl_2	DCE (55)	82.5 ± 4.4	26.4 ± 3.2	85	76 ± 4[b]
2	$CHCl_3$	DCE (55)	70.4 ± 3.3	39.6 ± 1.1	90	64 ± 3[c]
3	CH_2Cl_2	Br_2 (0.2)	14.1 ± 0.6	90.3 ± 2.2	46	13.5 ± 1
4	CH_2Cl_2	Br_2 (2.0)	8.0 ± 0.4	95.9 ± 2.0	37	7.7 ± 0.4
5	CH_2Cl_2	Br_2 (20)	3.1 ± 0.5	96.9 ± 2.0	20	3.1 ± 0.2
		B. Irradiation through a GWV Filter				
6	CH_2Cl_2	Br_2 (0.2)	3.1 ± 0.2	100.0 ± 2	160	3.0 ± 0.2
7	CH_2Cl_2	Br_2 (2.0)	2.5 ± 0.2	93.7 ± 2	67	2.6 ± 0.2
8	CH_2Cl_2	Br_2 (20)	1.1 ± 0.2	90.6 ± 2	27	1.2 ± 0.1
9	$CHCl_3$	Br_2 (2.0)	<0.5	105.0 ± 2	80	<1[c]

[a] General conditions: Solutions containing NBS (112 mM) and additives in either CH_2Cl_2 (1 mL, 15.5 mmol) or $CHCl_3$ (1 mL, 12.4 mmol) were placed in Pyrex NMR tubes and were irradiated through a Pyrex cold finger with or without a GWV filter until 85 ± 5% of the NBS was consumed at 15–18 °C. The brominated products were lost during evaporation. The best of two series of experiments and the maximum deviations of the two series are given. [b] This value was obtained by GC analysis, while others were obtained by NMR (400-MHz) analysis. In a separate injection, $CHBrCl_2$ was obtained in 5 ± 2% yields. [c] The initial heterogeneous solution became homogeneous as the reaction proceeded.

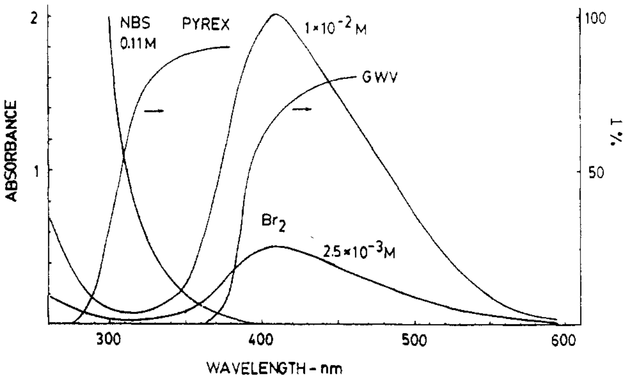

Figure 1. UV absorption and transmission spectra.

analysis.[18] However, using semiquantitative approaches and systematic variations in the reaction conditions, we have now clarified some basic reaction processes of NBS decompositions and found that a "hot" succinimidyl radical directly generated from photoexcitation of NBS is involved as the third radical chain carrier, which ring opens much more rapidly than the ground-state succinimidyl radical. We used cyclohexane and CH_2Cl_2 (or $CHCl_3$) as competing substrates, examining the pattern of the photodecomposition including the role of BPI under rigorously controlled irradiation conditions.

Accepted and noncontroversial reactions are listed in eq 2–8 to facilitate the presentation.

$$(CH_2CO)_2NBr\ (NBS) \xrightarrow{h\nu} (CH_2CO)_2N\cdot\ (S\cdot) + Br\cdot \tag{2}$$

$$RH + Br\cdot \rightarrow R\cdot + HBr \tag{3}$$

$$HBr + (CH_2CO)_2NBr \rightarrow (CH_2CO)_2NH + Br_2 \tag{4}$$

$$R\cdot + Br_2 \rightarrow RBr + Br\cdot \tag{5}$$

$$RH + (CH_2CO)_2N\cdot \rightarrow R\cdot + (CH_2CO)_2NH\ (SH) \tag{6}$$

$$R\cdot + (CH_2CO)_2NBr \rightarrow RBr + (CH_2CO)_2N\cdot \tag{7}$$

$$(CH_2CO)_2N\cdot \rightarrow \cdot CH_2CH_2CON{=}C{=}O\ (PI\cdot) \tag{8}$$

Results

In Figure 1, the absorption spectra of bromine and NBS are shown. It should be noted that the absorption minimum of bromine at ca. 320 nm coincides with the residual absorption of NBS from 300 to 380 nm. In view of the past general indifference to the photolysis conditions,[19] selectively filtered light sources were utilized to initiate the photodecomposition. When an NBS solution in CH_2Cl_2 or $CHCl_3$ was photolyzed in the presence of 1,1-dichloroethene (DCE), through a Pyrex filter, the major product was BPI in high yields (Table IA). Photolysis in the presence of bromine under the same irradiation conditions (Pyrex filter) gave much larger percentages of BPI than when the same solutions were irradiated through a GWV filter (Table IB), which allows the excitation of only bromine (Figure 1). It is noteworthy that significant BPI yields were obtained both in the presence of Br_2 and with $CHCl_3$ as the solvent (experiment 9) and that substantial differences in BPI yields could be caused by using either a Pyrex or a GWV filter in the photolysis of the NBS +

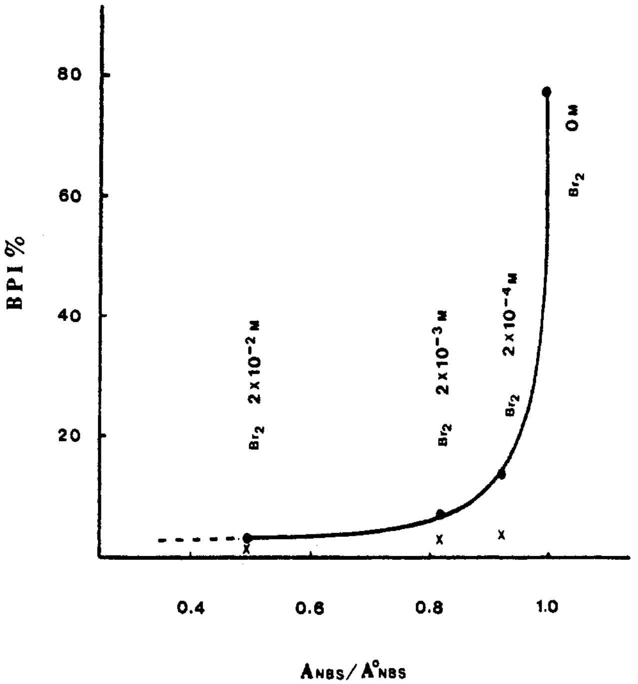

Figure 2. BPI percent yields vs. the fraction of incident light absorbed by NBS at various concentrations of bromine (10^{-4}–10^{-2} M). The corresponding BPI percent yields from Table IB (GWV filter) are marked by ×. $A°_{NBS}$ is the integrated absorbance of NBS and A_{NBS} that substracted from the absorbance of bromine.

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Table II. BPI Percent Yields from the NBS Decompositions in the Presence of Hydrocarbon Substrates and Bromine[a]

		$[C_6H_{12}]$ = 0.092 M		$[C_8H_{18}]$ = 0.065 M	
expt	Br_2, mM	BPI, mM	BPI, %	BPI, mM	BPI, %
		A. In CH_2Cl_2 Solvent			
10	0.2	24.3 ± 2.1	23 ± 2	11.3 ± 1.2	11 ± 1
11	2.0	21.0 ± 2.1	20 ± 2	8.1 ± 0.9	7.7 ± 0.8
12	20	10.5 ± 1.1	10 ± 1	2.1 ± 0.7	2.0 ± 0.6
13	200	1.7 ± 0.5	1.6 ± 0.4	...	...
14	0.25	43.1 ± 2.0	45 ± 2[c]		
15	4.0	36.9 ± 1.3	36 ± 1[c]		
16	20	30.7 ± 1.4	30 ± 1[c]		
17	100	25.9 ± 1.6	25 ± 1[c]		
		B. In $CHCl_3$ Solvent[b]			
18	0.2	16.5 ± 1.1	16 ± 1[c]	11.0 ± 1.3	11 ± 1
19	2.0	...	...	8.6 ± 1.8	8.2 ± 1.6
20	20	8.2 ± 1.2	8.0 ± 1.0[c]	2.0 ± 1.0	1.9 ± 0.8

[a] General conditions: Solutions containing solvent and NBS (112 mM) were irradiated through a GWV filter (experiments 10–13 and 18–20) or with RPR 3000-Å lamps (experiments 14–17) at 15–18 °C until 85 ± 5% of the NBS was consumed. Both C_6H_{12} (cyclohexane) and C_8H_{18} (hexamethylethane) were used in 1-mL aliquots. The best of two series of experiments and the maximum deviations from the two series are given. [b] Heterogeneous solutions before irradiation became homogeneous as the reaction proceeded. [c] These values were determined by NMR analysis, and the others by GC analysis. The GC peaks of the brominated products overlap with the solvent peak under the conditions used; their presence is shown by separate injection at lower temperatures.

Br_2 system. The former results are contrary to that reported previously.[6,7] In Figure 2, BPI percent yields were plotted against the fraction of incident light absorbed by NBS at various bromine concentrations to show the disproportionally higher yields of BPI by direct excitation of NBS (experiments 3–5) in comparison to those obtained by Br•-initiated reaction at the corresponding bromine concentrations (experiments 6–8). Because of this large discrepancy in BPI yields, all the Br•-initiated decompositions in the presence of bromine were irradiated through a GWV filter or a $NaNO_2$–sodium hydrogen phthalate filter solution (cutoff at 400 nm)[19] unless specified otherwise. As will be shown later, for comparisons of the percent BPI yield to be meaningful, the percent conversion of NBS has to be approximately the same because of bromine buildup under NBS + Br_2 photobromination conditions (Table IV).

Since BPI yields have been a contentious issue[9–11] a rigorous analytical method was established (see the Experimental Section). BPI readily reacted with a trace of water absorbed from the air to give, after decarboxylation, β-bromopropionamide (BPA) and CO_2; the reaction could be over in several minutes after exposure of the solution to the air. The integrated sum of the absorptions at 2250 cm^{-1} (BPI) and 2349 cm^{-1} (CO_2) was reasonably constant within experimental errors in a sealed cell. In spite of this, the estimated BPI percentages from the IR method were invariably lower than those obtained by the other two methods, probably due to CO_2 escaping during the solution transfer; this led to serious errors, particularly in the low range of BPI yields. Alternatively, BPI was deliberately decomposed by water during washings, and BPA was analyzed by NMR and/or GC methods. The NMR integration data were reproducible if the correct pulse sequence was used. In the GC and NMR analyses of BPI and other products, two to three readings were taken to obtain mean values. Because of losses during sample preparation, the actual yields could be higher than these figures.

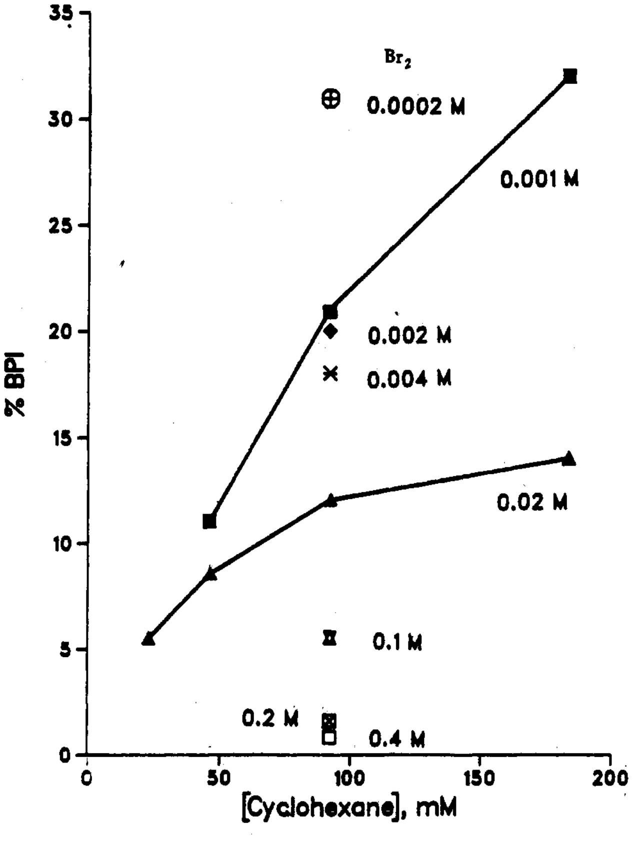

Figure 3. BPI percent yields vs. the concentration of cyclohexane in CH_2Cl_2 in the presence of various initial concentrations of bromine under the photolytic conditions (GWV filter) of Table IIA.

The effect of hydrocarbons on NBS decomposition was investigated next. For comparable series of NBS solutions shown in Table IB, the addition of cyclohexane (C_6H_{12}) or 2,2,3,3-tetramethylbutane (C_8H_{18}) caused dramatic increases in BPI percentages (Table II). Both cyclohexane and C_8H_{18} promoted higher yields of BPI with increasing concentrations, and the former did this with higher efficiency; but the higher the bromine concentrations, the lower the percentages of BPI obtained. This trend was similar in both CH_2Cl_2 and $CHCl_3$ solutions. It is noteworthy that, even in the presence of these hydrocarbons, $[Br_2] > 10$ mM could reduce the BPI yield to <2%. These relations are shown more clearly in Figure 3 in which the BPI percent yields determined under comparable conditions and in the presence of wider ranges of bromine and cyclohexane concentrations are summarized. The BPI percent yields at a fixed concentration of cyclohexane (92 mM, Figure 3) are also replotted against $[Br_2]$ in Figure 4, group A. For comparison, similar solutions containing NBS, bromine, and cyclohexane corresponding to exper-

Table III. H Abstraction Selectivity from Cyclohexane and CH_2Cl_2 in the Photolysis of NBS[a]

expt	C_6H_{12}, mM	$CHBrCl_2$, mM	$C_6H_{11}Br$, mM	SH,[c] mM	BPI, %	T, min	*r*
1	9.20	2.44 ± 0.3	1.61 ± 0.02	36 ± 0.2	69 ± 3	90	200
2	27.6	2.12 ± 0.12	3.68 ± 0.09	36.6 ± 0.8	67 ± 3	80	170
3	46.0	2.09 ± 0.06	7.10 ± 0.09	42.4 ± 0.7	66 ± 4	73	210
4	92.0	1.87 ± 0.02	11.0 ± 0.02	45 ± 2.0	61 ± 3	60	180
5	276	1.14 ± 0.03	21.8 ± 0.5	53 ± 0.7	56 ± 2	47	190
6	4600[b]	tr	26.1 ± 0.5	49.0 ± 1.1	8.6 ± 0.9[d]	135	

[a] General conditions: Solutions containing CH_2Cl_2 (1 mL, 15.5 mmol), DCE (60 mM), and NBS (112 mM) were photolyzed through a Pyrex filter at 15–18 °C until 85 ± 10% of the NBS was consumed. Because of interference from the CH_2 signals of BPI and BPA, the estimation of the NBS CH_2 signal contained large percentage errors. The second series of experiments gave *r* values of 180–210. [b] This experiment used CH_2Cl_2 (0.5 mL, 7.75 mmol), NBS (0.055 mmol), and DCE (0.028 mmol). The reaction was heterogeneous throughout the irradiation; reproducibility was poor. [c] The SH yields contain the fraction of unreacted NBS. [d] This BPI yield was determined by NMR, and the others were determined by GC analysis.

Table IV. H Abstraction Selectivity from Cyclohexane and CH_2Cl_2 for the NBS + Br_2 Reaction System[a]

Br_2,[b] mM		NBS, %							
init	obsd	conversn	$CHBrCl_2$, mM	$C_6H_{11}Br$, mM	$C_6H_{10}Br_2$, mM	SH,[d] mM	BPI,[e] mM	BPI, %	*r*
				A. Irradiation of Br_2[c]					
0.75	2.07	39	14.7 ± 0.9	6.88 ± 0.26	2.35 ± 0.06	32.9	9.60 ± 0.01	22.6	19
0.75	2.35	53	17.9 ± 1.0	6.99 ± 0.21	3.56 ± 0.04	46.0	12.0 ± 0.6	20.7	18
0.75	3.04	73	24.5 ± 0.5	8.27 ± 0.13	5.77 ± 0.35	67.1	12.7 ± 0.4	15.9	18
1.03	1.77	27	10.2 ± 1.8	4.63 ± 0.16	1.44 ± 0.25	23.5	5.76 ± 0.04	19.7	17
1.03	2.31	45	17.2 ± 1.1	6.21 ± 0.19	3.46 ± 0.15	39.7	9.85 ± 0.08	19.9	17
1.03	3.42	77	27.2 ± 1.2	8.34 ± 0.19	7.32 ± 0.09	70.4	14.2 ± 0.05	16.8	18
21.7	22.5	28	14.6 ± 0.1	5.70 ± 0.57	2.68 ± 0.12	26.1	4.25 ± 0.01	14.0	17
21.7	23.9	56	23.7 ± 0.2	7.55 ± 0.25	5.63 ± 0.11	54.1	7.03 ± 0.01	11.5	17
21.7	24.5	65	27.7 ± 1.0	7.23 ± 0.75	8.24 ± 0.20	64.2	7.29 ± 0.11	10.2	17
86.2	85.0	44	18.5 ± 1.4	9.24 ± 0.17	4.19 ± 0.08	44.6	3.21 ± 0.11	6.6	22
86.2	84.9	61	26.3 ± 1.8	9.74 ± 0.40	8.65 ± 0.35	63.3	4.31 ± 0.20	6.4	22
173	172	26	12.8 ± 1.5	6.28 ± 0.19	2.50 ± 0.08	27.1	1.7 ± 0.2	6.0	20
173	173	67	35.0 ± 0.4	10.2 ± 0.3	10.3 ± 0.3	73.0	2.3 ± 0.2	3.1	19
200		21	12.4 ± 0.7	5.70 ± 0.24	2.11 ± 0.08	21.9	1.33 ± 0.33	5.7	19
				B. Irradiation of NBS[f]					
0.83	1.85	30.6	8.55 ± 0.63	5.10 ± 0.12	1.06 ± 0.03	18.0	15.7 ± 0.5	46.5	20
0.83	2.19	47.4	12.2 ± 0.2	6.35 ± 0.13	2.03 ± 0.04	30.0	22.2 ± 0.5	42.5	19
0.83	2.58	68.1	17.6 ± 0.3	7.27 ± 0.13	3.37 ± 0.07	42.7	32.2 ± 1.1	43.0	17
21.8	25.3	25.5	8.86 ± 0.22	5.04 ± 0.25	1.23 ± 0.06	17.9	10.1 ± 0.5	36.1	20
21.8	26.7	55	19.8 ± 0.3	8.83 ± 0.09	4.15 ± 0.05	40.3	20.2 ± 0.8	33.4	18
21.8	26.8	74	24.1 ± 2.8	7.53 ± 1.13	5.27 ± 0.29	56.9	24.5 ± 1.0	30.1	15

[a] General conditions: Unless specified otherwise, solutions containing CH_2Cl_2 (1 mL, 15.5 mmol), cyclohexane (92 mM), and NBS (112 mM) were degassed with nitrogen and photolyzed for 10–35 min. The brominated products were determined by GC analysis. [b] The Br_2 concentration was determined by UV spectroscopy. [c] The first three experiments used $NaNO_2$–sodium hydrogen phthalate solution as a filter, and the others used a GWV filter. [d] The SH concentration was calculated from the amounts of NBS conversion and BPI formation. [e] The BPI concentration was determined as BPA by 100-MHz NMR analysis. [f] The samples were irradiated with Rayonet RPR 3000-Å lamps.

iments 10–13 were photolyzed with a 300-nm light source (Rayonet RPR 3000 Å) to primarily photoexcite NBS (Table II, experiments 14–17; Figure 4, group B). Similar irradiation with [Br_2] >100 mM was not attempted since the absorbance of Br_2 at 300 nm was as much as that of NBS at 112 mM, and the source of the BPI percent yields became ambiguous owing to extensive excitation of Br_2.

The type of radical chain carriers involved in the chain propagation was studied by determining the relative selectivity of intermolecular H abstraction between two substrates, cyclohexane and CH_2Cl_2. The products were analyzed by GC, and the selectivity of H abstraction from substrates was calculated by eq 9b, where $C_6H_{10}Br_2$ is

$$r = \frac{k_{C_6H_{12}}}{k_{CH_2Cl_2}} \text{ (per hydrogen)} = \frac{\ln [([C_6H_{12}] - [C_6H_{11}Br] - [C_6H_{10}Br_2])/[C_6H_{12}]]}{6 \ln [([CH_2Cl_2] - [CHBrCl_2])/[CH_2Cl_2]]} \tag{9a}$$

$$\text{or} = \frac{\ln [([C_6H_{12}] - [C_6H_{11}Br] - [C_6H_{10}Br_2])/[C_6H_{12}]]}{6[CHBrCl_2]/[CH_2Cl_2]} \tag{9b}$$

trans-1,2-dibromocyclohexane, which was obtained under the bromination conditions of the Br_2 + K_2CO_3 and NBS + Br_2 systems but not under those of the NBS + DCE system. The integrated eq 9a is approximated to eq 9b by the expansion[20] of the denominator in which the yields of $CHBrCl_2$ are low. For photolysis of NBS + DCE in CH_2Cl_2 (Pyrex filter) with increasing concentrations of cyclohexane, the selectivity was that due to H abstraction by the succinimidyl radical (S·) and varied from 170 to 210 in a random fashion (Table III). As expected, BPI yields decreased as cyclohexane concentrations increased, since S· was intercepted by cyclohexane more frequently. In the low concentration range of cyclohexane (experiments 1 and 2), the yields of $CHBrCl_2$ and $C_6H_{11}Br$ were low and much smaller than those of succinimide, even after the correction for unreacted NBS. While the error margins of this data must be fairly high, they were included in Table III since the *r* values did not deviate significantly from experiments 3–5. The poor material balance of brominated products

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(20) (a) Thaller, W. A. In *Methods in Free Radicals*; Huyser, E. S., Ed.; Dekker: New York, 1969; Vol. 2, pp 143–146. (b) If the conversion of substrates is low, the simple equation as used in previous publications (ref 5–14) can apply. In this paper, use of this equation would cause negligible error in *r* values if the percent yields of bromocyclohexanes are <5%. (c) Skell, P. S.; Traynham, J. G. *Acc. Chem. Res.* **1984**, *17*, 160.

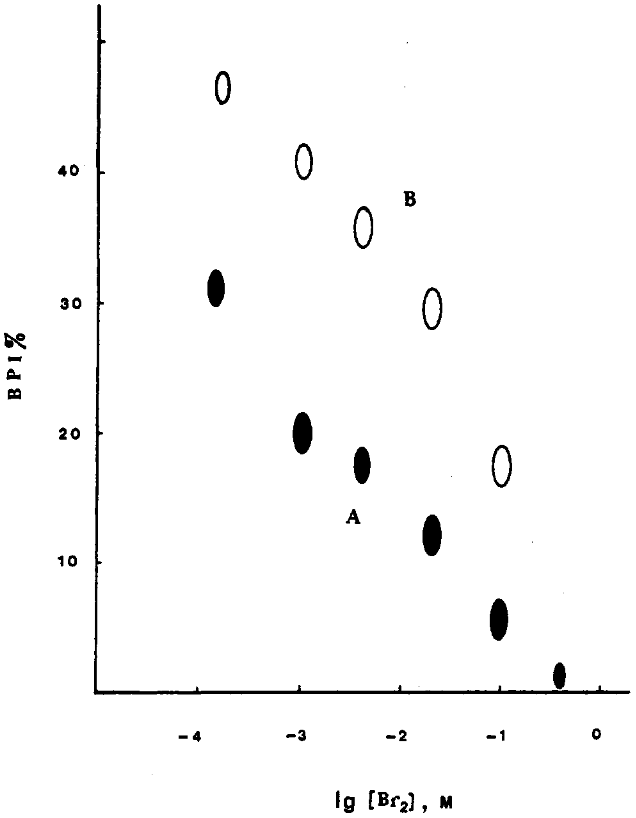

Figure 4. BPI percent yields vs. the initial bromine concentrations under >380-nm (solid ellipses, group A) and 300-nm irradiation (hollow ellipses, group B). Each ellipse represents two to five determinations with the spread of data shown by size.

was also reported by other groups[10,13] and might be attributed to the trapping of $CHCl_2\cdot$ radicals by DCE. However, a search by GC–MS failed to show the presence of such addition products.

The selectivity of Br·-induced H abstraction was determined by irradiation of bromine in the presence of anhydrous potassium carbonate. In preliminary experiments without stirring of reaction mixtures, the *r* values were found to vary from 18 to 20. When heterogeneous mixtures were stirred during irradiation, *trans*-1,2-dibromocyclohexane was also obtained if the $C_6H_{11}Br$ yields were >4 mM and the *r* values were calculated to be 15–18 (Table V). The facile formation of the vicinal dibromocyclohexane at a low concentration of $C_6H_{11}Br$ with respect to $[C_6H_{12}]$ is undoubtedly owing to a substantial neighboring group participation from the β-bromo substituent of $C_6H_{11}Br$ in the H-abstraction process by a bromine atom; this reaction has been thoroughly discussed by Skell and Traynham.[20c]

The bromine atom initiated bromination in the presence of NBS was carried out by irradiation of NBS + Br_2 with a light source >380 nm (GWV filter) or >400 nm ($NaNO_2$–sodium hydrogen phthalate filter solution). As the percent conversion of NBS increased, the observed $[Br_2]$ increased from the initial values and the BPI percent yields decreased concurrently (Table IVA). While BPI percent yields decreased as $[Br_2]$ increased, the *r* values varied randomly within experimental error in the range of 17–22, which is essentially that of the Br·-initiated bromination. These experiments were run at least twice to ascertain the reproducibility. The increment of $[Br_2]$ was significant when the initial $[Br_2] \leq 1$ mM but became smaller as the initial $[Br_2]$ increased and eventually became almost negligible even at high conversions of NBS. It was also shown that the *r* values varied within this range under other conditions, e.g., cyclohexane concentrations of 23–92 mM with $[Br_2] = 20$ mM.

Table V. H Abstraction Selectivity of Bromine Atoms from Cyclohexane and CH_2Cl_2[a]

Br_2, mM	$CHBrCl_2$, mM	$C_6H_{11}Br$, mM	$C_6H_{10}Br_2$, mM	*r*
6.6	3.5 ± 0.2	1.8 ± 0.1	0.13 ± 0.05	16
30	5.0 ± 0.4	2.2 ± 0.2	0.64 ± 0.02	16
27	16.0 ± 1.4	6.0 ± 0.1	2.08 ± 0.02	15
70[b]	17.5 ± 0.1	8.0 ± 0.1	2.35 ± 0.20	18
70	30.2 ± 0.8	11.8 ± 0.4	4.68 ± 0.12	17

[a] General conditions: Heterogeneous mixtures containing CH_2Cl_2 (4 mL, 62 mmol), cyclohexane (92 mM), Br_2, and K_2CO_3 (ratio of the last two compounds 1:5) in a UV cell were purged with nitrogen and irradiated through a GWV filter under magnetic stirring for 10–30 min. [b] The light source was a PEK 212 lamp (150 W) filtered through Corning filter CS-052 and $NaNO_2$–phthalate solution (cutoff <400 nm).

When similar solutions containing Br_2 and NBS were photoexcited with RPR 3000-Å lamps (emission at 300 nm), the BPI percent yields (Table IVB) became much larger than the corresponding yields obtained by Br· initiation (Table IVA), but they were still smaller than that obtained with the NBS + DCE system (Table III). Under the irradiation conditions, NBS was preferentially photoexcited particularly in low NBS conversions, and Br· was also generated by two sources, i.e., the photodissociation of NBS and that of Br_2 due to its weak absorption in the 300-nm region (see Figure 1). Solutions with $[Br_2] > 20$ mM were not used, since the absorbance of Br_2 at 300 nm became very high. Obviously, the rearrangement of $S\cdot \rightarrow PI\cdot$ (eq 8) occurred to a lesser extent because of some competing reactions from Br_2 and/or Br·, causing lower BPI percent yields (Table IV) than those brominations in which they were scavenged (Table III). It was noteworthy that while the BPI percent yields decreased steadily as the bromine concentration increased, the *r* values remained relatively insensitive to the increases in both series in Table IV. This will be discussed later in connection with the nature of the chain carriers.

The rates of bromination of the substrates by Br_2 + K_2CO_3 and by NBS + Br_2 were compared by selectively irradiating Br_2 with the >380- or >400-nm light source under comparable conditions for quantum yield measurements (Table VI). Two uncertainty factors were involved in the irradiation of the Br_2 + K_2CO_3 system: (i) light quanta might be reflected by heterogeneous mixtures; (ii) $[Br_2]$ in the former system decreased as the reaction progressed. These two uncertainties were alleviated by a high concentration of bromine in which incident light was absorbed efficiently with near constancy over the reaction duration. Assuming the quantum yield of bromination by Br_2 + K_2CO_3 as unity, that by NBS + Br_2 was higher by 60–80% and reproducible. The *r* values from these experiments were in good agreement with those presented in Tables IV and V.

Discussion

Experiments 1 and 2 in Table IA restate the well-known fact that NBS photodecomposition in the presence of an olefin (which contains no readily abstractable CH bonds) to scavenge Br_2 and Br· gives an excellent yield of BPI.[4,10,11] In other words, S· is generated from photoexcitation of NBS and ring opens to afford BPI and also propagates the chain process according to the mechanism shown in eq 2 and 6–8.[21]

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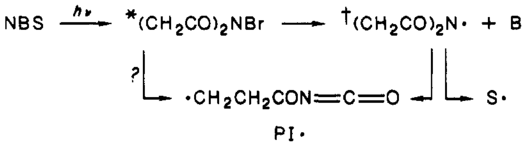
[21] (a) Johnson, H. W.; Bublitz, D. E. *J. Am. Chem. Soc.* **1958**, *80*, 3150. (b) Martin, J. C.; Bartlett, P. D. *J. Am. Chem. Soc.* **1957**, *79*, 2533.

Table VI. Comparisons of Rates of Bromination with Br_2 + K_2CO_3 (1:5) and Br_2 + NBS[a]

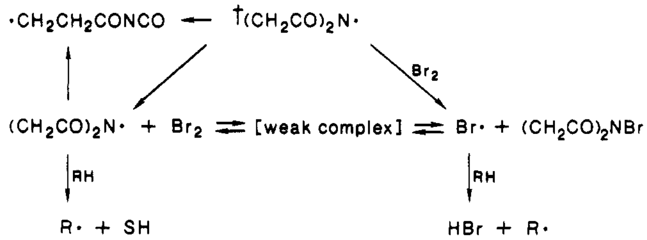
additive	$CHBrCl_2$, mM	$C_6H_{11}Br$, mM	$C_6H_{10}Br_2$, mM	$\sum(RBr)$[d]	r
K_2CO_3[b]	11.4 ± 2.2	5.95 ± 1.43	0.86 ± 0.13	19.09	17
NBS[b]	18.4 ± 4.4	9.55 ± 1.74	3.06 ± 0.25	34.07	21
K_2CO_3[c]	13.8 ± 0.3	6.19 ± 0.28	1.09 ± 0.05	21.45	15
NBS[c]	18.4 ± 0.1	9.66 ± 0.70	2.98 ± 0.04	34.02	21

[a] General conditions: Solutions containing CH_2Cl_2 (4 mL, 62 mmol), Br_2 (66 mM), cyclohexane (92 mM), and an additive in a UV cell (1 cm) were degassed and irradiated through filtered light emitting from a PEK 212 lamp (150 W) under the same conditions noted before. The ratio K_2CO_3:Br_2 = 5; [NBS] = 110 mM. The heterogeneous K_2CO_3 + Br_2 system was magnetically stirred. [b] These two samples were irradiated for 10 min with the light source filtered through a GWV filter. The conversion of NBS was 28%, and the BPI yield was 3.0 ± 0.2 mM. [c] These two samples were irradiated for 14 min with the light source filtered through $NaNO_2$–sodium hydrogen phthalate solution (cutoff >400 nm). The conversion of NBS was 26%, and the BPI yield was 2.9 ± 0.2 mM. [d] The sum of brominated substrates in which the yield of $C_6H_{10}Br_2$ was multiplied by 2.

Scheme I



Scheme II



There is no doubt that Br· initiates the decompositions of NBS (which is not photoexcited) to generate S· (i.e., Br· + NBS → Br_2 + S·) and thence BPI even with $CHCl_3$ as solvent, where Cl_3C· is involved as a propagating species.[7] The yields are dependent on the bromine concentration and also on the concentration of the alkane substrates and their susceptibility to H abstraction (Figures 3 and 4, group A). Particularly in the low-[Br_2] range (<20 mM), the BPI precursor S· is rapidly generated by the Br· initiation (Table II).

The data in Table II and Figures 2–4 demonstrate graded suppression of the BPI percent yields with increasing [Br_2] regardless of Br_2 or NBS being excited; the same conclusion can be deduced from Tables I and IV in the absence and presence of hydrocarbon substrates. It is particularly noteworthy from Figure 2 that the presence of [Br_2] = 0.2 mM is effective in reducing the BPI percent yields by several fold. If the BPI percent yields are taken as the extent of the S· concentrations generated during the reaction, these data imply that S· is rapidly scavenged by Br_2 even at [Br_2] ~1 mM regardless of the mode of generation under both types of irradiation conditions; the difference in BPI yields between the two will be discussed later. In the Br·-initiated reactions in Figures 2–4, the rate of Br· generation (therefore the generation of S·) must remain nearly constant at [Br_2] >5 mM (i.e., nearly the same amount of incident light >380–400 nm is absorbed by Br_2; see Figure 1); the steady decrease in BPI percent yields is a good indication that S· is scavenged by Br_2, i.e., the equilibrium in Scheme II (vide infra) is promoted to the right at higher bromine concentrations. The *r* values in the presence of bromine (Table IV) are also drastically reduced from 170–190 in Table III in agreement with the lack of S· reactivities.

The extra amounts of BPI in experiments 3–5 in comparison with the corresponding experiments 6–8 in Table I and those shown in Figure 2 are undoubtedly generated from direct excitation of NBS through an excited-state dissociation. This is further supported by a comparison of the BPI yields under 300- and 380-nm irradiation in Table IV; the direct generation of S· resulted in large increases of the BPI yield over that of the Br·-initiated (thermal) reaction. But the question arises whether the succinimidyl radical generated by direct excitation can be trapped by bromine even at [Br_2] >20 mM. It is proposed that excited NBS dissociates rapidly to give a succinimidyl radical carrying residual vibrational energy (†S·), which promotes a fast ring-opening process to give PI· in competition with relaxation and other processes (Scheme I). The lifetime of the photolytically generated †S· can be estimated to be <1 ns by assuming that the reaction rate constant of †S· + Br_2 and S· + Br_2 (see Scheme II) is just about that of a diffusion-controlled one (e.g., 10^{10} M^{-1} s^{-1}). Failure to detect the ESR signals of thermally relaxed S· in NBS photolysis by continuous or flash excitation supports this estimate.[22] If the lifetime of the vibrationally excited †S· is shorter than the subnanosecond scale, then Scheme I essentially merges with the direct formation of PI· from excited-state NBS.

Most photodecompositions reported in recent years[5–16] were carried out with a Pyrex filter;[19] therefore, the reported BPI yields must contain certain fractions derived from direct excitation of NBS even in the presence of Br_2 as shown in Figure 2. Tanner's[11–13] and Walling's[10] groups have demonstrated that Skell's claims[5–9,14] of nil BPI yields under comparable conditions are inaccurate. However, notwithstanding the theoretical prediction of symmetry correlations,[23] the formation of BPI in photolysis through a Pyrex filter can hardly be useful to distinguish between the imidyl radical configurations because of the extraneous source of BPI. This paper demonstrates that BPI is formed by Br·-initiated decomposition of NBS whether carried out in CH_2Cl_2 or $CHCl_3$ and that the BPI yields are an indicator of the extent of S· generation. The crucial question is the most recent controversy over the existence of another chain carrier in addition to Br· and S· in propagating the bromination in the NBS + Br_2 system.[13,14]

Table IV exhibits an unusual feature in that with over 200-fold increases in [Br_2] the BPI percent yields decrease steadily, but the range of *r* values is essentially that of Br·-propagated reactions (Table V) by either method of irradiation. The latter practically negates the involvement of another radical propagating the bromination of the substrates in the NBS + Br_2 system. The agreement of *r* values in Table IV (parts A and B) demonstrates that whether the NBS decomposition in the presence of Br_2 is initiated by Br· or by photoexcitation of NBS, it largely involves Br· as the chain carrier in intermolecular H abstraction. It follows that S·, regardless of the mode of generation, quickly undergoes two competing reactions, i.e., ring opening to PI· and trapping by Br_2 (the same for †S·) as shown in Scheme II. The *r* values of 16–21 in Table IVB

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[22] Our own as well as others' (e.g., K. U. Ingold, private communication) efforts have not been able to detect the ESR signal of S· from NBS photolysis. Dr. J. C. Scaiano informed us that pulsed-laser (N_2, 8-ns) flash photolysis has not successfully yielded an S· transient.

[23] (a) Koenig, T.; Wielsek, R. A. *Tetrahedron Lett.* **1975**, 2007. (b) Dewar, M. J. S.; Olivella, S. *J. Chem. Soc., Chem. Commun.* **1985**, 301.

and the corresponding high BPI percentages support this proposal, which also implies that intermolecular H abstraction from the substrates (CH_2Cl_2, cyclohexane) by S· is much slower relative to these two processes; i.e., the S· propagation processes do not contribute significantly, and the Br· propagation processes essentially dominate the bromination of the substrates. In Br·-initiated decomposition (Table IVA), the *r* values of 17–22 and the graded decreases in BPI percentages with the increases in [Br_2] suggest that the equilibrium in Scheme II shifts to the right as [Br_2] increases, causing lower concentrations of S· in the reaction system.

The relative quantum efficiency of bromination by Br_2 + K_2CO_3 and Br_2 + NBS is certainly different, but the increases for the latter are too small to be significant in such chain reactions where the chain length also affects this quantity. In the present experiments, the concentrations of Br_2 and Br· (i.e., quantum input) were maintained as constant as could be in both series to obtain a meaningful comparison. The small increase in quantum efficiency may be attributed to, at best, the fact that Br· is aggregated or weakly complexed in different ways in the two systems; its reactivity is somewhat modified in the intermolecular H abstraction, but its selectivity remains essentially that of Br· in both systems. We conclude *that the photodecomposition of the NBS + Br_2 system is propagated by S· and Br· as the reactive intermediates without the necessity of involving another radical intermediate.*

The dynamics of the equilibrium are governed by the concentrations of chain carriers, Br_2 and NBS, and also by the susceptibility of substrate CH bonds toward abstraction.[24,25] Photolysis of NBS and Br_2 in the presence of the reactive substrate toluene afforded only benzyl bromide but no BPI. It is known that the Br· chain process dominates this reaction because Br·-induced H abstraction is especially facile.[26-29] This facility may arise from a complex formation of Br· with the aromatic nucleus in analogy to the modification of Br· reactivity in aromatic solvent.[30] 2,2,3,3-Tetramethylbutane has inert primary CH bonds that are susceptible to S· attack but not to Br·; the equilibrium must be shifted to S·, which undergoes H abstraction and BPI formation. This is probably the reason why large percentages of BPI are obtained in its presence (Table II).

Cyclohexane has CH bonds susceptible to Br·-induced H abstraction,[11] which generates the C_6H_{11} radical and, in turn, S· by bromine transfer as in eq 10. In Br·-initiated

$$\mathrm{RBr} + \mathrm{Br}\cdot \xleftarrow[k_2]{\mathrm{Br}_2} \mathrm{C_6H_{11}}\cdot \text{ or } \mathrm{C_8H_{17}}\cdot \xrightarrow[k_1]{\mathrm{NBS}} \mathrm{S}\cdot + \mathrm{RBr} \qquad (10)$$

bromination (Figure 3; Table II) the effects of adding cyclohexane no doubt cause high BPI yields through this route. The increases of BPI yields are much larger at [Br_2] = 1 mM than at [Br_2] = 20 mM; this supports the alternative route of generating S· at low concentrations of Br_2. However, in the vicinity of [Br_2] = 20 mM, the BPI yield remains as high as 8–10% as shown in Tables II and IV. This is surprising in view of the ratio of bromine-transfer processes by Br_2, and NBS is calculated to be higher than 100 in favor of the former (eq 10). This is calculated by taking a conservative value[4,31] of $k_1/k_2 = 1/500$, [Br_2] = 20 mM, and the maximum [NBS] = 100 mM. Walling et al.[10] also have reported an abnormally high ring-opening rate of S· in the presence of cyclohexane. The discrepancy implies that k_1/k_2 is probably larger than that estimated;[31] this is also suggested by the following argument.

The formation of bromine during the photodecomposition of NBS has been known without a satisfactory explanation.[5-7,13] Under either irradiation condition, a significant increase in observed bromine concentrations at lower initial [Br_2] (e.g., ~1 mM) suggests that Br· generated by Br_2 or NBS photolysis reacts with NBS to give Br_2 (Scheme II), which would be an additional source of [Br_2] in Table IV. In the range of a high ratio of [NBS]/[Br_2], PI· and R· preferentially react with NBS in the subsequent bromine-transfer process (eq 7 and 10), leaving a molecule of Br_2 as an additional buildup in the system. At higher [Br_2] (e.g., >50 mM), bromine transfer primarily occurs by reactions with Br_2 (eq 5 and 10); as a molecule of Br_2 is concurrently consumed, [Br_2] remains at the same level (see Table IV). It is surprising that even a initial [Br_2] = 20 mM, the bromine concentration does increase with the progress of bromination. From Table IV, taking [Br_2] = 10 mM and [NBS] = 100 mM as the concentrations where the rates of bromine transfer are about the same for both reagents, the ratio of k_1/k_2 in eq 10 is calculated to be 1/10, much larger than that estimated before[31] and quoted subsequently.[4]

The investigation of the photodecomposition of NBS has been treated as a straightforward radical chain problem without due consideration of excited-state chemistry. Two aspects of the photodecomposition of NBS in the presence of Br_2 require comment, that is, the possible sensitization processes as shown in eq 11 and 12. There is good reason

$$^*\mathrm{Br}_2 + \mathrm{NBS} \rightarrow \mathrm{Br}_2 + {}^*\mathrm{NBS} \rightarrow \mathrm{S}\cdot + \mathrm{Br}\cdot \qquad (11)$$

$$^*\mathrm{NBS} + \mathrm{Br}_2 \rightarrow \mathrm{NBS} + {}^*\mathrm{Br}_2 \rightarrow 2\mathrm{Br}\cdot \qquad (12)$$

to believe that excited NBS possesses a lifetime $<10^{-9}$ s from the failure to detect it by nanosecond flash-excitation techniques.[22] Thus, reaction 12 is rather unlikely. The energy transfer of excited- state Br_2 to NBS (reaction 11) is not likely, owing to unfavorable energetics. Further, it is known that excitation of Br_2 causes rapid predissociation[32] to give Br·; excited-state Br_2 is likely a short-lived species.

Finally, the present discussions assume without evidence that the succinimidyl radical is derived from the excited state of NBS by a diabatic process as a hot species possessing residual energy (†S·; see Scheme I) and ring opens rapidly. The energy level of the lowest singlet excited state of NBS (assuming the photodissociation from this state) is estimated to be 87 kcal/mol (at 330 nm), and the bond dissociation energy *D*(N–Br) in NBS is generously estimated[13] to be 50 kcal/mol. As the diabatic dissociation of singlet excited-state NBS should leave ~30 kcal of the residual energy to S· and Br·, it is entirely possible that †S· can be an electronically excited-state succinimidyl radical, in view of low-energy gaps (15–20 kcal/mol) estimated from theoretical calculations.[33] If this is the case,

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[24] Traynham, J. G.; Lee, S. Y. *J. Am. Chem. Soc.* **1974**, *96*, 3590.

[25] Day, J. C.; Lindstrom, M. J.; Skell, P. S. *J. Am. Chem. Soc.* **1974**, *96*, 5616.

[26] Walling, C.; Rieger, A. L.; Tanner, D. D. *J. Am. Chem. Soc.* **1963**, *85*, 3129.

[27] Russell, G. A.; Desmond, K. M. *J. Am. Chem. Soc.* **1963**, *85*, 3139.

[28] Pearson, R. E.; Martin, J. C. *J. Am. Chem. Soc.* **1963**, *85*, 3142.

[29] Incremona, J. H.; Martin, J. C. *J. Am. Chem. Soc.* **1970**, *92*, 627.

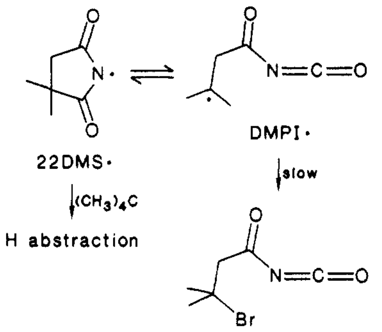
[30] Russell, G. A. *J. Am. Chem. Soc.* **1958**, *80*, 4987, 4997.

[31] Skell, P. S.; Tuleen, D. L.; Readio, P. D. *J. Am. Chem. Soc.* **1963**, *85*, 2850.

[32] Kistiakowski, G. B.; Sternberg, J. C. *J. Chem. Phys.* **1953**, *21*, 2218.

[33] (a) Clark, T. *J. Am. Chem. Soc.* **1979**, *101*, 7746. (b) Apeloig, Y.; Schreiber, R. *J. Am. Chem. Soc.* **1980**, *102*, 6144. (c) Dewar, M. J. S.; Pakiari, A. H.; Pierini, A. B. *J. Am. Chem. Soc.* **1982**, *104*, 3242.

Scheme III



there is another aspect of succinimidyl radical chemistry to be investigated in the future.

Delineation of Recent Controversies

On the basis of the results, we shall attempt to resolve the lingering controversies published[13,14] since this paper was submitted. The recent joint paper[13] by Tanner's and Walling's groups concluded that competing propagation processes by S· and Br· could reasonably explain all the existing data but *could not convincingly demonstrate experimentally the absence of a third propagating species in the NBS + Br_2 system.* On the other hand, using new sets of data and arguments obtained from the photodecomposition of 2,2-dimethyl-*N*-bromosuccinimide (22DMNBS), Skell and co-workers[14] have reiterated that in the NBS + Br_2 system the propagation by Br· and S· can hardly explain the overall results and that *another radical chain carrier must exist but its identity and structure are unknown*; *the* Π *radical configuration has been withdrawn.*[14]

Undoubtedly, the controversy originates from the failure to recognize the enhanced ring-opening process of †S· derived from direct photolysis of NBS (see Scheme I) and the equilibrium of Scheme II. Reference 13 has reexamined various experiments under Skell's previous conditions. In ref 13, the conspicuous omission of fast reactions of †S·, particulary that of †S· → PI·, in the reaction scheme for the quantitative analysis of BPI yields and *r* values should result in inconsistency in the observed and predicted values as shown in Figures 3 and 4; similarly, it applys to the conclusion drawn in appendix 2 of ref 14.

Though we did not use 22DMNBS for photodecomposition, "the ridiculuous yields of 12000–32000% for the ring-opened isocyanate, $(CH_2)_2CBrCH_2CONCO$", extrapolated in ref 14 can be reconciled on the basis of Schemes I and II of this paper. The extraordinarily high yields of the isocyanate in Table III of ref 14 most likely arise from direct photolysis of 22DMNBS to give the enhanced ring opening of †22DMS· in analogy to our observation in the presence of an olefin. Owing to a slow bromine atom transfer reaction of the *tert*-alkyl radical center of DMPI· (Scheme III), the chain length must be short and the majority of the isocyanate should be derived from †DMS·. However, the unusually low yields of the isocyanate in photolysis in the presence of Br_2 (<3%, Table IV of ref 14) are very surprising and, at best, might be attributed to the generation of the ground-state 22DMS· and the slow bromine transfer processes of DMPI· (Scheme III). There is no evidence to indicate nor reason to believe[5] that the ring opening of 22DMS· is *irreversible* as claimed by Skell's group.[14] The data of Tables III and IV in ref 14 are most likely derived from two different reaction species (i.e., different reactivity) and cannot be extrapolated in either direction.

Conclusion

The photodecomposition of NBS under various conditions with selective excitation provides experimental proof of the following new insights: (1) Photoexcitation of NBS affords extraneous BPI, which is assumed to be derived from a vibrationally "hot" †S· by the enhanced ring-opening process in competition with relaxation to ground-state S· and other processes. (2) It is established that Br· reacts with NBS to provide ground-state S· and Br_2, and the reaction is reversible, establishing equilibrium rapidly. (3) The formation of extra Br_2 in the photodecomposition of NBS or NBS + Br_2 is attributed to this reaction. (4) The relative reactivity (*r* value) is dependent on $[Br_2]$, and, therefore, also varies with the extent of NBS decompositions; the comparison of *r* values is meaningful only when $[Br_2]$ and/or the fraction of NBS decomposition is comparable. (5) Ground-state S· also ring opens to give BPI, but with a slower rate than †S·; the use of BPI yield as a reactivity indicator requires careful control of irradiation wavelengths. (6) The Br·-initiated decomposition of NBS in the NBS + Br_2 system involves no other radicals than Br· and S· propagating the intermolecular chain bromination if only Br_2, but not NBS, is photoexcited; the photoexcitation of NBS involves a third radical (†S·) in addition to these two propagating species.

Experimental Section

Chemicals. Dichloromethane (Fisher, ACS) was purified by distillation over P_2O_5 (99.9% pure by GC analysis). Chloroform (Fisher, certified ACS grade) was shaken five times with about half its volume of water and then dried over anhydrous magnesium sulfate for 1 h, followed by distillation over P_2O_5 before use (99.8% pure by GC analysis). *N*-Bromosuccinimide (BDH, reagent grade) was recrystallized from water and dried over $CaCl_2$; together with bromine (Anachemia, reagent grade) they were kept in a desiccator. Hexamethylethane (Aldrich, 99%) was used as supplied. Cyclohexane (Fisher, spectroanalyzed grade) and 1,1-dichloroethene (DCE; Aldrich, 99%) were distilled prior to the experiments. Anhydrous potassium carbonate (BDH, analytical grade) was ground and dried under vacuum at 150 °C for 24 h. Argon (Union Carbide Linde, 99.9995%) was used as supplied.

General Procedure for the Photodecomposition of NBS. In an NMR tube (Wilmad, 505 ps) or a 1-cm UV cell was placed NBS (ca. 20 or 80 mg), and the tube was wrapped with aluminum foil. Subsequent operations before irradiation were carried out in a dark place. An aliquot of freshly prepared standard bromine solution in CH_2Cl_2 was added, followed by a substrate, cyclohexane, or 2,2,3,3-tetramethylbutane. The vessel was covered with a septum and was purged with argon through Teflon needles for about 5 min. As soon as the first few bubbles escaped from the solution, the vessel was put into an ice–salt bath. After degassing, the vessel was shaken to give a homogeneous solution. The vessel was irradiated in a water bath (18 ∓ 3 °C) by placing it about 3 cm from the light source, which was a 200-W Hanovia medium-pressure mercury lamp placed in a Pyrex cold finger with or without a GWV filter (cutoff at 385 nm). For 300-nm photolysis, a Rayonet photochemical reactor equipped with RPR 3000 lamps was used, and the NMR tubes were cooled in a water bath (15–17 °C). At intervals, the percent conversion of NBS was monitored with a Varian EM360 or Bruker SY100 spectrometer. When the reaction was stopped, the UV absorption of photolysates was recorded to calculate the bromine concentration.

BPI Analysis. After irradiation, the BPI yield was analyzed by one of the following methods:

(A) The photolysate, which was placed in a flask wrapped with aluminum foil, was evaporated under vacuum at 15–18 °C, and the residue was dissolved with 4 mL of CH_2Cl_2. The solution was washed with 5% $NaHSO_3$ (0.4–0.8 mL). The residue of the aqueous layer was extracted with CH_2Cl_2, and the organic layers were dried with $MgSO_4$. The filtrate was concentrated for GC analysis with a Hewlett-Packard 5792A equipped with an HP3990 integrator and an OV-1 capillary column (HP, 12.5 × 0.20 mm). The percentage yield of BPA was determined by normalization calculation using molar response factors of BPA and succinimide. Typical set of retention times (160 °C, 10 psi): succinimide, 1.27 min; BPA, 1.46 min.

(B) A measured amount of photolysate was evaporated as above. The residue was dissolved in $CDCl_3$ for FT-NMR analysis with a Bruker WH400 spectrometer.

For a control experiment, a $CDCl_3$ solution containing succinimide (ca. 2 mg), NBS (ca. 2 mg), and bromine (2.5×10^{-2} M) was placed in two NMR tubes inside a dark hood. After 5 min, one tube was emptied into a 5-mL flask wrapped in aluminum foil and was evaporated. The glass part of the Rotavapor was covered with black paper. The residue was taken up with $CDCl_3$ (0.8 mL) and transferred back to the NMR tube. Two tubes were analyzed by NMR to give an identical ratio of $I_{2.96}/I_{2.76}$ (the intensities at 2.96 and 2.76 ppm). In order to obtain accurate peak height, caution was exercised in choosing NMR parameters so that the second pulse always began only after the protons in question relaxed totally from the excited state resulting from the first pulse: protons on 5-mm ^{13}C probe, ~25° pulse, SF = 400.134 395 6 MHz, SI = 32K, SW = 4000.000 Hz, AO = 4.096. The BPI percentage was calculated according to $(I_{3.63} + I_{2.81})/(I_{2.76} + I_{3.63} + I_{2.81})$, where $I_{3.63}$ and $I_{2.81}$ stand for the intensity of the triplet of BPA at 3.63 and 2.81 ppm (J = 6.62 Hz), respectively, and $I_{2.76}$ is the intensity of the singlet of succinimide at 2.76 ppm. The percentage conversion of NBS was calculated according to $I_{2.96}/(I_{2.96} + I_{3.63} + I_{2.81} + I_{2.76})$ where $I_{2.96}$ stands for the intensity of the singlet of NBS at 2.96 ppm.

(C) The BPI yields in Table IV were determined with a Bruker SY100 (100 MHz) as follows. The measured amount of photolysate was added with a measured volume of *p*-bromotoluene (0.1 M in CH_2Cl_2), and the resultant mixture was evaporated. The residue was taken up in $CDCl_3$ (0.7 mL), and the NMR spectrum was recorded. The integration of the triplet at 3.65 ppm for BPA was compared with that of the singlet of *p*-bromotoluene at 2.31 ppm (standard) to calculate the concentration of BPA. From the percent conversion of NBS and the BPI concentration, the yield of succinimide was calculated. Control experiments showed that before and after the evaporation ca. 2% of the *p*-bromotoluene was lost with respect to succinimide.

For each experiment, two tubes of solutions were photolyzed, and mean values and errors were obtained. For each reaction, two to three readings were obtained, and standard deviations were calculated. Each series of experiments was repeated, and maximum deviations from mean values are given in the tables.

Other Product Analyses. The yields of $CHBrCl_2$, cyclohexyl bromide ($C_6H_{11}Br$), and *trans*-1,2-dibromocyclohexane ($C_6H_{10}Br_2$) were determined with GC. $CHBr_3$ was chosen as an internal standard. The molar response factor of cyclohexyl bromide to $CHBr_3$ was obtained by analyzing standard mixtures in various ratios. It was assumed that the molar response factor of $C_6H_{10}Br_2$ was the same as that of $C_6H_{11}Br$. The photolysate was washed with 10% $NaHSO_3$ and then was dried with $MgSO_4$, followed by the addition of $CHBr_3$ (1–3 μL). The filtrate was used for the determination of *r* values. Typical sets of the retention times (min) were as follows: $CHBrCl_2$ 1.84, $CHBr_3$ 4.84, cyclohexyl bromide 9.40 at 55 °C and 8 psi; $CHBr_3$ 1.25, cyclohexyl bromide 1.55, succinimide 1.84, $C_6H_{10}Br_2$ 2.84 under temperature programming of 120–200 °C, 10 °C/min at 8 psi. The yield of succinimide was determined with GC. Benzophenone as the internal standard was added prior to injection to the sample prepared by method B. The molar response factor of succinimide was obtained by analyzing graded standard mixtures. The typical set of the retention times were for succinimide 1.27 min and for benzophenone 5.87 min at conditions of 160 °C and 10 psi. The collection of data and the evaluation of errors were the same as described above. When the yields of $C_6H_{10}Br_2$ were >3 mM, two small minor peaks closely attached to the major peaks were noticed. GC–MS analysis of these peaks showed that the major peak showed a mass spectral pattern identical with that of *trans*-1,2-dibromocyclohexane and the minor peaks were probably isomers of the dibromide.

Relative Rates of Bromination. A solution containing the reactants was purged with nitrogen and was irradiated with a PEK 212 150-W high-pressure mercury lamp filtering through Corning filter CS-052 (7380) and $NaNO_2$–sodium hydrogen phthalate solution (1-cm thickness) to give >400-nm light; alternatively, the light source was filtered with a GVW filter to give >380-nm light. Two solutions containing NBS + Br_2 and Br_2 + K_2CO_3 were irradiated under the same conditions for the same duration, and the yields of brominated products were determined as described above. The solution of Br_2 + K_2CO_3 was heterogeneous and was magnetically stirred.

Bromination of Toluene with NBS and Br_2. Solutions containing CH_2Cl_2 (1 mL), toluene (0.09 M), NBS (0.11 M), and bromine (2×10^{-4}–2×10^{-2} M) were photolyzed through a GWV filter as above until 90 ∓ 5% of the NBS was consumed. The photolysates were worked up in the usual manner for GC analysis, which showed only benzyl bromide as the product but no BPA.

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Deuterium Isotope Effects on the Oxygen Atom Transfer Reactions of α-Azo Hydroperoxides

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Cyclic α-azo hydroperoxide **1** (*cis*-3-bromo-4,5-dihydro-5-hydroperoxy-4,4-dimethyl-3,5-diphenyl-3*H*-pyrazole) and acyclic α-azo hydroperoxide **2** [(4-methoxyphenyl)(phenylazo)methyl hydroperoxide] were converted to the ROOD analogues **1**-*d* and **2**-*d*. The reactions of **1** and **1**-*d* in $CDCl_3$ at 34 °C with amines, diphenyl sulfide, and 2,3-dimethyl-2-butene yielded the corresponding amine oxides, sulfoxides, and epoxides in better than 90% yields. The reactions were found to be of the first order in both hydroperoxide and substrate (second order overall). Deuterium isotope effects (k_H/k_D) of 1.3 ± 0.1 were found for the oxidation of the three types of substrate. The reactions of **2** and **2**-*d* with benzyl methyl sulfide and 2,3-dimethyl-2-butene, carried out in C_6D_6 at 34 °C, produced the corresonding sulfoxide and epoxide in 90%+ yields. As expected, the reactions were of the second order overall (first order in hydroperoxide) in the aprotic medium. Values of k_H/k_D of 1.3 ± 0.1 were found for these oxidations. The mechanistic implications of these results are discussed.

The chemistry of organic hydroperoxides is often considered to deal largely with free-radical formation and the related metal ion catalyzed decompositions. An additional property of hydroperoxides is their ability to transfer ox-

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