Radical Chain Carriers in *N*-Bromosuccinimide Brominations
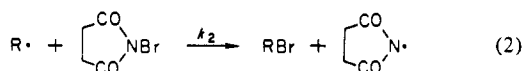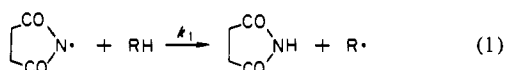
Cheves Walling,* **Gamil M. El-Taliawi,[1]** **and Chengxue Zhao[2]**

Contribution from the Department of Chemistry, University of Utah, Salt Lake City, Utah 84112. Received June 16, 1982

Abstract: Relative reactivities per hydrogen (r's) for neopentane–CH_2Cl_2 have been redetermined for photobromination by Br_2, $r = 0.03$–0.4, NBS + Br_2, $r = 1$–2.5, and NBS + 1,1-dichloroethylene (DCE) as a Br· trap, $r > 20$. In the last case β-bromopropionyl isocyanate (BPI) is the major product. In Br_2 reactions r's vary with experimental conditions and are increased significantly by a number of carbonyl and succinimide derivatives. BPI is also a major product in the bromination of $CHCl_3$ in the presence of DCE and in the UV photolysis of NBS in CD_2Cl_2 even in the presence of Br_2. For CH_2Cl_2–CD_2Cl_2 mixtures, $k_H/k_D \simeq 10$ for both NBS–Br_2 and NBS–DCE systems. The kinetics of decomposition of NBS in CH_2Cl_2 in the presence of Br_2, initiated by UV light, azobis(isobutyronitrile) and benzoyl peroxide are zero order in NBS, with k for attack of the chain-carrying radical on CH_2Cl_2 estimated as 55 at 50 °C. In the presence of DCE, benzoyl peroxide initiated reactions in CH_2Cl_2 are also zero order, with rates corresponding to a rate constant for ring opening $k_d \simeq 1660$. Addition of cyclohexane produces an unexpected increase in rate corresponding to $k_d \simeq 1.5 \times 10^4$, and k for reaction of the succinimide radical with cyclohexane $\simeq 10^4$. If these rate constants are valid, they require a radical lifetime of $\sim 10^{-4}$ s, and this and their low value appear inconsistent with a high-energy excited state of the succinimide radical. It is proposed that the chain carrier in the NBS–Br_2 system is a reaction product of NBS and a bromine atom, for which some possible structures are suggested.

In 1942 Ziegler reported that *N*-bromosuccinimide (NBS) was a convenient brominating agent, particularly for conversion of olefins to allylic bromides.[3] Although the reaction was quickly recognized as a free radical chain process[4–6] and has become a standard synthetic procedure, the actual chain carriers involved have been the subject of recurrent controversy.

By the mid 1970's it was generally accepted that the original Bloomfield mechanism[4] involving the succinimide radical as chain carrier with chain-propagating steps (1) and (2) was easily ob-

$$\underset{CO}{\overset{CO}{\bigg]}}N\cdot \; + \; RH \; \xrightarrow{k_1} \; \underset{CO}{\overset{CO}{\bigg]}}NH \; + \; R\cdot \qquad (1)$$

$$R\cdot \; + \; \underset{CO}{\overset{CO}{\bigg]}}NBr \; \xrightarrow{k_2} \; RBr \; + \; \underset{CO}{\overset{CO}{\bigg]}}N\cdot \qquad (2)$$
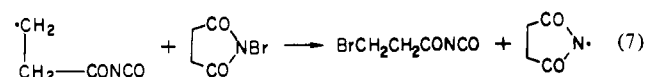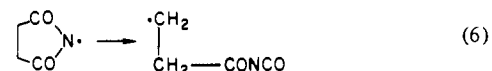
servable[7,8] only with unreactive substrates such as saturated hydrocarbons, preferably in the presence of halogen atom traps, e.g., olefins lacking reactive allylic hydrogens,[8] a technique which had previously shown to be effective in eliminating halogen atom reactions in alkyl hypohalite halogenations.[9] On the other hand, in allylic and benzylic brominations (eq 3 and 4), the conditions

$$Br\cdot \; + \; RH \; \xrightarrow{k_3} \; HBr \; + \; R\cdot \qquad (3)$$

$$R\cdot \; + \; Br_2 \; \xrightarrow{k_4} \; RBr \; + \; Br\cdot \qquad (4)$$
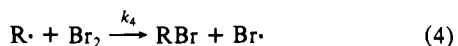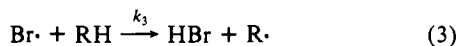
under which NBS is most commonly used, the reaction was believed to occur through a bromine atom chain as originally suggested by Goldfinger,[10] the NBS simply acting as a Br_2 source via the rapid reaction

$$HBr \; + \; NBS \; \rightarrow \; Br_2 \; + \; succinimide \qquad (5)$$
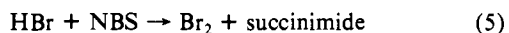
Actually the two processes have not proved easy to distinguish, since they predict similar kinetics and the chain carriers have not been observed by any spectroscopic technique. The usual recourse has been to relative reactivity data for pair of substrates, assuming a bromine atom chain when these were the same as in photobromination with Br_2 alone (as in the case of allylic and benzylic substrates[11–14]) and a succinimide radical chain when there were marked differences (saturated aliphatics and other unreactive substrates[7,8]). In unreactive media, particularly in the presence of olefin traps, the intermediacy of the succinimide radical was further supported by the competing formation of β-bromopropionyl isocyanate (BPI).[15,16] presumably via a competing β scission (eq 6 and 7). In cases where intermediate or variable relative reactivities were observed, it might be assumed that competing Br· and succinimide radical (S·) chains were occurring simultaneously.

$$\underset{CO}{\overset{CO}{\bigg]}}N\cdot \; \longrightarrow \; \underset{CH_2-CONCO}{\overset{\cdot CH_2}{\big|}} \qquad (6)$$

$$\underset{CH_2-CONCO}{\overset{\cdot CH_2}{\big|}} \; + \; \underset{CO}{\overset{CO}{\bigg]}}NBr \; \longrightarrow \; BrCH_2CH_2CONCO \; + \; \underset{CO}{\overset{CO}{\bigg]}}N\cdot \qquad (7)$$

The subject has been reopened by Skell in a series of papers beginning in 1978.[17–20] In these he examined the ring-opening reaction (6) in more detail for a number of succinimide and glutarimide derivatives, showing that its ease of occurrence varied in a plausible manner with ring strain and resonance stabilization of the resulting radical and that, in the case of NBS, the opening was reversible. He also simultaneously examined relative re-

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(1) Visiting professor; Cairo University, Cairo, Egypt.
(2) Visiting scientist; Institute of Organic Chemistry, Shanghai, People's Republic of China.
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Table I. Br_2 Photobrominations of Neopentane–CH_2Cl_2[a]

	mmol of					
expt no.	CH_2Cl_2	neo-C_5H_{12}	Br_2	% react	r	remarks
1a	7.73	2.32	3.84	26.4	0.057	
1b				48.2	0.046	
1c				58.2	0.030	
1d				67.3	0.028	
1e				77.0	0.027	
2	26.8	2.0	2.0	86	0.193	+10 mmol of $(CF_3CO)_2O$
3	26.8	2.0	1.0	90	0.53	+4 mmol of benzoic anhydride
4	26.8	2.0	1.0	33.2	0.39	+2 mmol of succinimide
5	26.8	2.0	1.0	15.8	0.45	+1.78 mmol of N-phenylsuccinimide

[a] 50 °C, visible light initiation unless indicated.

Table II. NBS Brominations of Neopentane–CH_2Cl_2[a]

	mmol of						
	NBS	CH_2Cl_2	C_5H_{12}	additive	% react	BPI, %	r
1	0.0815	7.81	0.285	0.081 DCE	100	72	>20
2	0.104	7.74	0.213	0.017 DCE	100	75	>20
3	0.145	7.77	0.98		100	60	nd
4	0.166	7.77	0.555		15	nd	19.2
5	2.0	18.23	2.0	0.036 Br_2	91	nd	1.73
6	0.39	8.38	1.67	0.194 Br_2	100	0	1.7
7	0.104	7.81	5.56	0.163 Br_2	100	0	1.04
8	0.142	7.59	0.508	0.106 Br_2	53	nd	2.5

[a] UV initiation, 15 °C unless indicated.   [b] Visible light.

activities (most thoroughly of the neopentane–CH_2Cl_2 pair) and BPI yields with NBS alone, in the presence of Br· traps (ethylene, *tert*-butylethylene, and 1,1-dichloroethylene) and with small quantities of added Br_2·, concluding that the data were inconsistent with simple competing S· and Br· chains.

Since it will be important later, we will repeat his basic argument. Defining r as the relative reactivity per hydrogen of neopentane to CH_2Cl_2, i.e., for low conversion experiments

$$r = [C_5H_{11}Br][CH_2Cl_2]/6[C_5H_{12}][CHCl_2Br] \qquad (8)$$

from Skell's data, r is 0.1 for photobromination with Br_2 alone[17] and is 17 for NBS in the presence of Br· traps,[19] although the major product (85–95%) under these conditions is BPI. For NBS in the presence of small amounts of Br_2, r was reported as 1.15.[17] Were this the consequence of competing Br· and S· chains, simple calculation indicates that they are occurring at about equal rates and the BPI yield should be cut in half (or reduced even less if (6) is reversible since the resulting open radical can also react with the Br_2 present[21]). However, no BPI whatsoever was detected under these conditions.

A plausible way of reconciling these results is to assume the possibility of some third chain carrier in the NBS–Br_2 system, and Skell has done this by proposing that the succinimide radical can exist in two electronic states, a ground state, S_π·, and excited state, S_σ·. In the presence of Br_2, S_π· is the carrier, formed by reaction 4 followed by eq 9.

$$Br· + NBS \rightarrow S_\pi· + Br_2 \qquad (9)$$
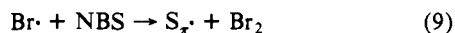
Reaction 9 is considered reverisble, and it is proposed that S_π· is also formed by the reaction of resonance-stabilized carbon radicals (CCl_3, allylic and benzylic radicals) with NBS. On the other hand, for more reactive radicals (primary and secondary radicals, $CHCl_2$), reaction with NBS is sufficiently exothermic to generate S_σ·, the only species assumed able to undergo the ring opening reaction (6) leading to BPI or to give addition to olefinic or aromatic systems.

Although the proposal was consistent with the brief results initially presented,[17,18] we decided to examine some of the same systems independently, since the data were striking and the

proposed interpretation unusual.[22] This paper reports our initial results. While we confirm a number of Skell's findings and our results also seem to rule out simple competing S· and Br· chains, some of them, particularly rate measurements, also seem inconsistent with the S_σ·–S_π· model, and some alternatives are considered.

The Neopentane–CH_2Cl_2–Br_2 System. A mixture of the three components were irradiated and products analyzed by gas–liquid chromatography (GLC) or NMR. Relative reactivities per H (r's) were calculated from eq 8 or its integrated form where appropriate. Five experiments analyzed by GLC gave r's of 0.02–0.09, and a single experiment (experiment 1 in Table I) run in a sealed tube and periodically analyzed by NMR shows a small drift in r with conversion. We thus confirm that CH_2Cl_2 is perferentially attacked. In fact our values of r, although they show some scatter, are actually lower than that Skell reports (0.1). Two runs using CD_2Cl_2 gave r's of 0.35 and 0.115, indicating a substantial kinetic isotope effect, although it cannot be given a precise value.

Interestingly, small quantities of a number of carbonyl compounds significantly increase r (Table I), including N-phenylsuccinimide and succinimide itself. In addition to the data in Table I, a number of other carbonyl compounds gave $r = 0.1$–0.4 with no obvious correlation with structure. In regard to the reaction in the presence of succinimide, we should note that no NBS is detectible by NMR on adding Br_2 to succinimide solutions, so eq 5 is not significantly reversible. However, on irradiation an orange solid precipitates which titration indicates has the approximate composition succinimide HBr· $^1/_2Br_2$. Similarly, passing dry HBr into a solution of succinimide in CH_2Cl_2 precipitates a white crystalline solid, with a composition of succinimide ·HBr.

Although our data raise some unanswered questions, they show that product distributions, from which apparent r's are calculated, can vary significantly with experimental conditions, a matter which will be important in our subsequent discussion.

NBS Reactions. Results of a number of representative competitive brominations of neopentane–CH_2Cl_2 by NBS alone and in the presence of 1,1-dichloroethylene (DCE) or Br_2 are listed

(21) The 1-bromo-2-methyl-2-butyl radical is estimated to react with Br_2 some 10^3 times as rapidly as with NBS.[18] See also: Skell, P. S.; Tuleen, D. L.; Readio, P. D. *J. Am. Chem. Soc.* **1963**, *85*, 2850–2851.

(22) Carbenes and O_2 may react from singlet and triplet states, and photochemistry is essentially the chemistry of excited states. However, unless there is some quantum mechanical barrier such as that to spin inversion prolonging their lines, bimolecular reactions of excited states of molecules with other substrates must occur at close to diffusion-controlled rates to be observed.

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Table III. NBS–CD$_2$Cl$_2$–Br$_2$ Reactions[a]

expt no.	mmol of			% react	BPI, %
	NBS	CD$_2$Cl$_2$	Br$_2$		
1	0.084	7.73	0.028	88	38.7
2	0.089	7.53	0.134	60	56.7
3	0.094	7.79	0.235	86	19
4	0.121	7.85	0.177	41	22.5
5	0.11	7.85	0.054	55	39.3
6[b]	0.114	7.73	0.076	100	2.5
7[c]	0.146	7.34	0.063	27	0

[a] UV initiation, 15 °C unless indicated. [b] Visible light, 15 °C. [c] AIBN (0.0175 mmol), 60 °C.

Table IV. NBS–Chloroform Reactions[a]

expt no.	mmol of			% react	BPI, %
	NBS	CHCl$_3$	additive		
1	0.105	6.2	0.088 DCE	100	81.0
2[c]	0.134	6.1	0.052 DCE	78	79[c]
3[e]	0.186	6.2	0.029 DCE	100	25
4	0.094	6.2		100	0
5	0.093	6.2	0.08 Br$_2$	100	0
6	0.109	6.2[b]	0.077 DCE	87	84
7[c]	0.146	6.2[b]	0.077 DCE	95	81
8	0.106	6.3[b]		100	7.5[d]
9	0.11	6.2[b]	0.10 Br$_2$	100	5.5[d]

[a] UV initiation, 15 °C unless indicated. [b] CDCl$_3$. [c] Visible light. [d] Estimated from IR spectrum. [e] 50 °C, initiated by 0.0173 M benzoyl peroxide.

Table V. Rates of NBS Bromination of CH$_2$Cl$_2$ in the Presence of Br$_2$[a]

run no.	[NBS]	[initiator]	[Br$_2$]	10^7 rate, M/s	$10^7 R_i$, M/s	λ
1	0.180	0.0876	0.106	62.9	2.14	29.4
2	0.179	0.0244	0.115	43.7	0.60	72.8
3	0.090	0.0874	0.068	64.4	2.14	36.1
4	0.178[b]	0.0874	0.095	6.92	2.14	3.2
5	0.206	0.080[c]	0.224	15.3	0.33	46.4

[a] At 50 °C, AIBN initiator unless indicated. [b] In CD$_2$Cl$_2$. [c] Benzoyl peroxide.

Table VI. Kinetics of NBS–DCE Bromination of CH$_2$Cl at 50 °C

run	[NBS]	[DCE]	[Bz$_2$O$_2$]	10^7 rate M/s	$10^9 R_i$, M/s	λ
1	0.229	0.0225	0.008 26	11.83	3.41	374
2	0.229	0.0225	0.001 65	7.68	0.68	1129
3	0.118	0.0113	0.008 26	12.58	3.41	369
4[a]	0.229	0.0225	0.008 26	12.76	3.41	374
5	0.229	0	0.008 26	11.25	3.41	330
6	0.207	0.185	0.015 1	7.70	6.21	124
7	0.230	0.054	0.005 8	7.03	2.4	293
8[b]	0.216	0.119	0.008 2	4.80	3.4	141
9[c]	0.180	0	0.006 6	17.4	2.7	645
10[d]	0.172	0.0226	0.008 26	166	3.41	4870
11[e]	0.229	0.0225	0.008 26	273	3.41	8006

[a] Not deoxygenated. [b] Undistilled DCE. [c] 0.059 M *tert*-butylethylene in place of DCE. [d] 0.33 M cyclohexane. [e] 0.92 M cyclohexane.

in Table II. Again, we qualitatively confirm Skell's observations. With DCE, neopentane is preferentially brominated, but the major product is BPI. With NBS alone, *r* is smaller, BPI yields are reduced, and solutions turn yellow, indicating the presence of Br$_2$. If Br$_2$ is added initially, no BPI is detected and *r* = 1–2.5. However, there are minor qualitative discrepancies. In the presence of DCE we find little or no CHCl$_2$Br, although, from analysis of known synthetic mixtures, an amount of CHCl$_2$Br, sufficient to give *r* = 17 would be easily measurable. Accordingly we can only state that from our own data *r* ≥ 20. On the other hand, succinimide yields are larger than can be accounted for by neopentyl bromide formed, and, in the presence of relatively high concentrations of DCE, e.g., experiment 2, the reaction mixture shows additional NMR peaks, δ 2.9 and 3.85, suggestive of some radical addition to the olefin. Evidently there are minor side reactions in addition to (1), (2), (6), and (7).

Attempts to determine the kinetic isotope effect in the NBS–Br$_2$ system by comparison of r's measured with CH$_2$Cl$_2$ and CD$_2$Cl$_2$ gave inconsistent results, so it was measured directly by competitive bromination of CH$_2$Cl$_2$–CD$_2$Cl$_2$ and analysis of the CH(D)Cl$_2$Br product by GLC–MS using the relative intensity of the *m/e* 83–84 peaks (CH(D)Cl$_2$$^+$). The result, k_H/k_D = 10.5, was confirmed by a combination of NMR and GLC analysis which gave k_H/k_D = 9.6–10.4. A similar determination for the NBS–DCE system gave very similar values, k_H/k_D = 10.6 (GLC–MS) and 10.0 (GLC–NMR).

Although no BPI is detected in the presence of Br$_2$ in any of the experiments in Table II, we obtain a different result in brominations of CD$_2$Cl$_2$ alone (Table III). With use of UV initiation we find substantial amounts of BPI even in the presence of large amounts of Br$_2$. However, the yield is decreased by using visible light, and none was detected in an experiment of 60 °C using azobis(isobutyronitrile) (AIBN) as initiator. A plausible interpretation of the UV experiments is that BPI can also be formed by direct photodissociation of NBS, see below.

Finally, since Skell has reported that the CCl$_3$· radical reacts with NBS to yield S$_π$· rather than S$_σ$·,[20] we have examined the NBS bromination of chloroform and deuteriochloroform (Table IV). Both, in our hands, give roughly 80% BPI in the presence of DCE, using either UV or visible light initiation (in the latter case the reaction is extremely slow as might be expected since no strongly light absorbing species is present), and some BPI is also

formed in benzoyl peroxide initiated reactions. With CDCl$_3$ and UV initiation, 5.5% BPI is even detected in the presence of added Br$_2$, which again may be a measure of the contribution of initial photodissociation.

Reaction Rates. A prominent feature of Skell's analysis is the postulate that S$_σ$· formed from NBS in the presence of olefin is a high-energy species which reacts with substrates or opens with *k*'s of 10^7–10^9 L/mol s while the ground-state species S$_π$· reacts more sluggishly. This difference should be reflected in overall reaction kinetics so we have carried out kinetic experiments following the rate of NBS disappearance in CH$_2$Cl$_2$ in sealed, degassed tubes, monitoring the reaction by disappearance of the NBS by NMR, and employing UV light, AIBN, or benzoyl peroxide as initiators. Initial experiments using UV initiation established that rates were reproducible, showing little or no induction period, and that kinetics in both NBS–Br$_2$ and NBS–DCE systems were zero order in NBS. In parallel experiments NBS–Br$_2$ reactions went some 3 times as fast as those using NBS–DCE and almost 100 times as fast as ones using Br$_2$ alone. With this done, attention was shifted to thermally initiated experiments in which rates of initiation could be estimated without recourse to quantum yield measurements.

Considering first reactions in the presence of Br$_2$, Table V and Figure 1 show that NBS consumption is again zero order in NBS, shows a large kinetic isotope effect, and, with AIBN initiated reactions, varies approximately with [AIBN]$^{1/2}$. These observations are all consistent with the usual expression for a chain halogenation in which the slow step in chain propagation is attack of the chain-carrying radical on substrate, here, CH$_2$Cl$_2$.

$$-d[NBS]/dt = k_{10}[RH](R_i/2k_t)^{1/2} \qquad (10)$$

If (10) is obeyed and the rate of chain initiation, R_i, is calculated from literature rate constants of initiator decomposition, 2.45 × 10^{-6} s^{-1} for AIBN[23] and 4.13 × 10^{-7} s^{-1} for benzoyl peroxide,[24]

(23) Peterson, R. C.; Markgrav, J. H.; Ross, S. D. *J. Am. Chem. Soc.* **1961**, *83*, 3819–3823. These appear to be the most precise data of many and refer to diphenylmethane as solvent. Rates, however, vary little with solvent.
(24) Bartlett, P. D.; Nozaki, K. *J. Am. Chem. Soc.* **1946**, *68*, 1686–1962. Data for unimolecular decomposition in benzene after correction for any induced reaction.
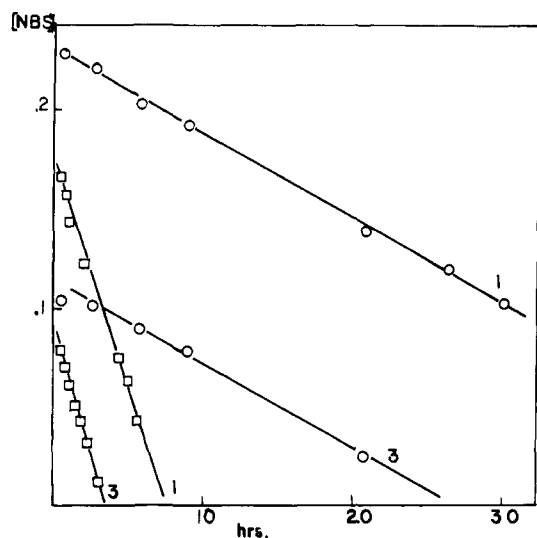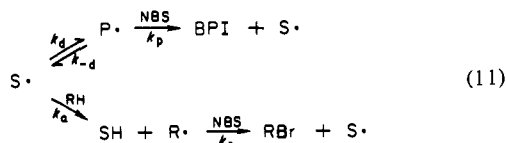
Figure 1. Kinetics of NBS brominations. Numbers correspond to runs in tables: squares, Table V; circles, Table VI.

assuming a fraction, f, of the initiator radicals escape from the solvent cage and start chains, kinetic chain lengths, $\lambda = \text{rate}/R_i$, can be calculated. The data assuming $f = 0.5$ are included in Table V. It is worth noting that the paired experiments 1 and 5 using AIBN and benzoyl peroxide initiator differ in rate by a factor of 4.12 quite close to the square root of the ratio of R_i's 2.54. This implies that f for the two initiators is indeed quite similar.

Table V indicates that chain lengths are quite short for thermally initiated NBS–Br$_2$ bromination and vary inversely with rate as eq 10 requires. If we assume that chain termination is essentially a diffusion-controlled reaction and set $k_t = 2 \times 10^9$, k_{10} can be estimated;[25] e.g., for experiment 1 $k_{10} = 55.1$. For all initiated experiments at 50 °C, $k_{10} = 55 \pm 8$ (standard deviation of mean). From experiments 1 and 4, $k_H/k_D = 9.1$ in good agreement with our directly measured value, and, taking $r = 1.15$ (Skell's value[17] and near the middle of our range), k_{10}(neopentane) $= 380$.

Analysis of brominations in the presence of DCE is more complicated. If we assume that reaction 11 is proceeding through

$$
\begin{array}{c}
\text{P·} \xrightarrow[k_p]{\text{NBS}} \text{BPI} + \text{S·} \\
k_d \nearrow \!\!\! \diagup\!\!\! \diagdown k_{-d} \\
\text{S·} \\
k_a \searrow \!\!\! \diagup \text{RH} \\
\text{SH} + \text{R·} \xrightarrow[k_r]{\text{NBS}} \text{RBr} + \text{S·}
\end{array}
\qquad (11)
$$

competing ring-opening and hydrogen abstraction reactions of a succinimide radical, where P· represents the ring-opened species, even introducing the simplifying assumption that all k_t's are equal, i.e.

$$R_i = 2k_t([\text{S·}] + [\text{P·}] + [\text{R·}])^2 \qquad (12)$$

leads to a complex expression. However, if $k_r[\text{NBS}] \gg k_a[\text{RH}]$, $k_p[\text{NBS}] \gg k_d, k_{-d}$, i.e., reversibility of ring opening is minor and the slow steps are those involving k_a and k_d

$$-d[\text{NBS}]/dt = (k_d + k_d[\text{RH}])(R_i/2k_t)^{1/2} \qquad (13)$$

again an expression zero order in NBS.

When AIBN was employed as initiator at 50 °C, zero-order kinetics were observed, but chains were very short, only traces of BPI ($\sim$5%) were detected with the balance of the NBS consumed appearing almost entirely as succinimide. Further, detailed analysis of one run showed that, while AIBN disappeared at the

expected rate, little CHCl$_2$Br was produced (10%), and the major bromine-containing product identified was α-bromoisobutyronitrile, 30% based on NBS consumed or 46% based on AIBN decomposed. Although the reasons for these anomalies are unknown, it is concluded that AIBN was not a satisfactory initiator for kinetic studies.

Benzoyl peroxide yielded more tractable results, and data from a number of runs are listed in Table IV with some typical data plots in Figure 1. Reactions showed little or no induction period and were zero order in NBS with a somewhat less than square-root dependence on peroxide, and in all BPI was the major product. Several other variables were investigated. An undeoxygenated run 4 gave a small induction period but no subsequent retardation. Reactions are slightly slower at high DCE levels or when undistilled DE was employed. Substitution of *tert*-butylethylene for DCE gives a slightly higher rate, while omission of any olefin gives a similar rate to a low level of DCE but no BPI among the products. On the assumption that the highest rates represent the cleanest chains and that k_d, ring opening, is the major component of the slow step in eq 13, from runs 1, 2, 3, and 9, we calculate $k_d = 1660 \pm 200$ (standard deviation of mean) by using the same assumptions as before.

Addition of a more reactive substrate (cyclohexane) should produce a higher rate, since it provides an alternate path for chain propagation. Runs 10 and 11 show that this is the case, but the effect is much more than anticipated. Thus, analysis of the products from run 11 showed 58% BPI and 28% cyclohexyl bromide, from which the expected rate increase should be about 50%. The actual increase is a factor of 23, run 10, at a lower cyclohexane concentration, which gave 74% BPI and 20.3% cyclohexyl bromide showed a 14-fold increase. If we analyze runs 10 and 11 as before, partitioning the contribution of k_d and k_a on the basis of product yields, we get $k_d = 1.33$ and 1.70×10^4 and k_a(cyclohexane) 11 and 7.6×10^3. From a detailed analysis of neopentyl bromide–BPI yields as a function of neopentane concentration. Skell[19] has obtained k_a(neopentane)/$k_d = 0.087$ at 15 °C. Averaging our k_d's (1.52×10^4) and ignoring the temperature difference implies k_a(neopentane) $\simeq 590$, and with Skell's value of r (17×6/molecule), k_a(CH$_2$Cl$_2$) $\simeq 5.8$.

Discussion

As we have seen, most of our relative reactivity data on neopentane–CH$_2$Cl$_2$ are in reasonable quantitative agreement with those reported by Skell. Bromine alone selectively attacks CH$_2$Cl$_2$, and in fact, our values of r are even smaller than Skell reports (the larger values we find in the presence of certain additives will be considered later). NBS in the presence of DCE selectively brominates neopentane (here our r's are actually larger than Skell's), but the major product is BPI. Experiments using NBS in the presence of added Br$_2$ give intermediate values of r near unity but, generally, no BPI. Taken together, these results also demand two types of chain carrier in addition to simple bromine atoms and are consistent with the existence of S$_\sigma$· and S$_\pi$· radicals. The only NBS–Br$_2$ system in which we observe BPI in substantial yield is in the UV initiated bromination of CD$_2$Cl$_2$ alone. Our suggestion that this is the consequence of direct photolysis of NBS is supported by our kinetic results. From Table V, because of the large kinetic isotope effect the kinetic chain length of an AIBN initiated bromination of CD$_2$Cl$_2$ is only 3.2 at an observed rate of 6.9×10^{-7} M/s. In a typical experiment in Table III, 88% reaction occurred in 100 min, corresponding to a much higher rate, 2.64×10^{-5} M/s, and accordingly an even shorter chain, so that most of the NBS must have been consumed via initial photolysis. Scission of the N–Br bond in UV-photoexcited NBS should yield a succinimide radical with considerable excess energy, which might undergo immediate β scission, or alternatively, photoexcited NBS might undergo β scission followed by Br· loss: either path would account for our observations. If so, while they have no direct bearing on the nature of the propagating species in the chain reaction, the data in Table III indicate a possible complication in interpreting the results of UV-initiated NBS reactions at very high light intensities or in the absence of reactive

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(25) Fortunately, since $k_t^{1/2}$ appears in (10), a fourfold uncertainty (reasonable range) only introduces a twofold uncertainty in the calculation. Ingold has recently shown that for a number of unhindered amidyl radicals, k_t occurs at or near diffusion-controlled rates.[27]

substrates, even in the presence of Br· traps.

The only substantial disagreement between our product distribution studies and those of Skell[20] are in the NBS–CHCl3 system, Table IV, where we observe high yields of BPI in the presence of DCE. Since similar results are obtained with UV, visible light, and peroxide initiation, they cannot be due to nonchain photodissociation of NBS. We are at a loss to explain the discrepancy, but, if we are correct, our results indicate that the same succinimide radical is involved as in CH2Cl2 systems.

The major new data in our study are our kinetic results, and, since parallel NBS–DCE and NBS–Br2 experiments proceed at rather similar rates, much faster than with Br2 alone, they also appear to rule our competing S· and Br· chains in the NBS–Br2 system.

Our data on the NBS–Br2 system seem relatively straightforward and indicate a chain carrier which is more reactive than a simple bromine atom but still rather sluggish, $k(CH_2Cl_2) \simeq$ 55. In support of this approximate value, Skell[19] has reported a photochemical bromination of CH2Cl2 by NBS–Br2 in which a 0.16 M solution of NBS underwent 31% reaction in 2 h with a quantum yield of 9. Analyzing this result via eq 10 in the same way gives $k = 85$.

Our results on NBS–olefin systems are admittedly less clear-cut. For some reason, AIBN is a relatively inefficient initiator and produces little BPI (again, Skell reports that a reaction initiated by photodecomposition of AIBN gives a slow reaction and short chain length[19]) and with benzoyl peroxide initiation addition of cyclohexane leads to an unexpectedly large increase in rate. On the other hand, reactions are all zero order in NBS, indicating that reactions of the succinimide radical are involved in the rate-determining step, and the reactions are not first order in initiator as is usually characteristic of a strongly inhibited process.[26] The most plausible interpretation which we can given is that, in brominations of CH2Cl2 alone, some side reaction yields a relatively unreactive species but that this retardation is wholely or in part eliminated by the presence of cyclohexane. Some evidence that reactions in the presence of cyclohexane are, in fact, properly represented by eq 13 comes from recent literature data. Ingold[27] has examined the kinetics of halogenation of cyclohexane by *N*-chloro and *N*-bromo-*N*-ethylproponamide in the presence of trichloroethylene as bromine atom trap by essentially the same technique as ours and estimated k_a for the *N*-ethylpropionamidyl radical as 6400 at 28 °C. Similarly, Yip and Chow[28] have carried out the flash photolysis of *N*-bromo-3,3-dimethylglutarimide in cyclohexane and report $k = 3500$ for the reaction of the 3,3-dimethylglutarimidyl radical with cyclohexane near 25 °C. These numbers may be compared with our 50 °C value $\sim 10^4$. Finally, Skell[19] reports a quantum yield experiment in which a 0.16 M solution of NBS in CH2Cl2 containing *tert*-butylethylene was irradiated and gave a quantum yield of 67. From the reported optical densities the reaction followed a sigmoid curve, but the overall conversion, 82% in 90 min, corresponds to a rate of 2.43 $\times 10^{-5}$ M/s. Assuming that the major product was BPI, we would calculate $k_d = 2550$, intermediate between our values in the presence and absence of cyclohexane.

Taken at their face value, all these results indicate that the succinimidyl radical present in olefin-containing systems undergoes ring opening with a rate constant of not over 2×10^4, while rate constants for H abstraction from saturated hydrocarbons are substantially smaller. Unless much higher rates can in fact be demonstrated, there seems to be no good basis for assuming that the rate constants actually lie in the range of 10^7–10^9 as has been proposed.[19] This, in turn, introduces difficulties in the assumption that the sucinimide radical present under these conditions is a highly reactive excited state. First, rate constants for H abstraction actually overlap those for the NBS–Br2 system, so while there

is clearly a difference in selectivity, there is little evidence for higher reactivity (other than ring opening) for the proposed S_σ radical. Second, if the major reaction is ring opening with $k_d \simeq 10^4$, the *lifetime* of the S_σ· radical must be $> 10^{-4}$ s which seems implausibly long for an excited state in the absence of any obvious quantum mechanical "forbiddeness" of its collapse to the ground state. Third, the large kinetic isotope effect we find in the presence of DCE, $k_H/k_D = 10.6$ seems inconsistent with a strongly exothermic process with an early transition state. In contrast, k_H/k_D for chlorine atom reactions range from 1.3 (toluene) to 2.7 (ethane).[29] Similarly, k_H/k_D for hydroxyl radical attack on acetone is only 3.54.[30] Further, the similarity of k_H/k_D's for NBS reactions in the presence of DCE and Br2, if it is not purely fortuitous, implies a similarity in energetics and transition-state structure which parallels the similarity in rate. The alternative, which we favor, is that the chain-propagating species in the presence of Br· traps is, in fact, the ordinary ground-state succinimide radical, with a reactivity in H abstraction similar to that of *N*-ethylpropionamidyl and 3,3-dimethylglutarimidyl radicals, plus the ability to undergo rapid ring opening of its somewhat strained ring. Since the N–H bond formed in all these H abstractions is generally considered to be quite strong, so reactions should be exothermic, these low rates are surprising. However, unexpected barriers to other hydrogen abstractions also exist.[31]

This leaves open the question of the chain carrier in NBS–Br2 systems which plainly has quite different properties from either S· or Br· in the absence of NBS. If the succinimide radical is not involved,[32] the most plausible alternative is some species derived from Br· which must necessarily be present in the system. At this point, we can only suggest two possible schemes. One (eq 14)

is the sequence which effectively converts Br· to a type of alkoxy radical which is known to attack C–H bonds at relatively high rates.[33] It was with this in mind that the brominations using Br2 in the presence of a variety of carbonyl compounds (Table I) were examined. Although r's approaching those in the NBS–Br2 system were observed, we failed to find any corresponding increase in rate so the results are inconclusive. We should also note a severe restriction on this formulation: since the activation energies for H abstractions by Br· are only about 2 kcal more than ΔH for the reactions, the overall HBr addition to the NBS carbonyl (the first two steps in (14)) would have to be an exothermic process in order to produce a significant increase in rate.[34] The second possibility is some sort of interaction of Br· with the Br of NBS, e.g., eq 15. Here it is difficult to formulate the second step, but

(26) See, for example: Bartlett, P. D.; Altshul, R. *J. Am. Chem. Soc.* **1945**, *67*, 812–822.

(27) Sutcliffe, R.; Anpo, M.; Stolow, A.; Ingold, K. U. *J. Am. Chem. Soc.* **1982**, *104*, 6064–6070.

(28) Yip, R. W.; Chow, Y. L.; Beddard, C. *J. Chem. Soc., Chem. Commun.* **1981**, 955–6.

(29) For these and other examples cf: Huyser, E. S. "Free Radical Chain Reactions"; Wiley-Interscience: New York, 1970; p 106.

(30) Walling, C.; El-Taliawi, G. M. *J. Am. Chem. Soc.* **1973**, *95*, 844–847.

(31) Peroxy radicals are a notable example. Although the reaction of the *tert*-butylperoxy radical with toluene is slightly exothermic, the rate constant at 30 °C is only 0.012, Howard, J. H. In "Free Radicals"; Kochi, J. K.; Ed.; Wiley: New York, 1973; Vol II, p 21.

(32) As evidence for S_σ· under these conditions, Skell has reported that *N*-iodosuccinimide + I2 gives the same ratio of halides in competitive halogenation as does NBS–Br2. However, the only experiment reported[19] gave only a 2.5% yield of products on 3.5-h irradiation—in view of the lack of evidence for a chain reaction and the well-known instability of alkyl iodides on irradiation, this experiment seems unconvincing.
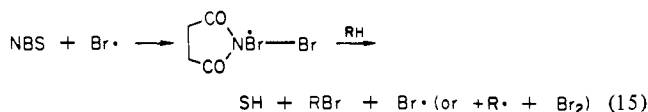
(33) Paul, P.; Small, R. D., Jr.; Scaiano, J. C. *J. Am. Chem. Soc.* **1978**, *100*, 4520–7.

(34) The formation of a crystalline succinimide–HBr adduct may have some bearing on this question, and we also find evidence for interaction between NBS and molecular Br2. NBS is quite soluble in liquid Br2, and, in this solvent its proton NMR signal is shifted downfield relative to CH2Cl2, while its IR carbonyl peak shifts to lower frequency.

$$NBS + Br\cdot \longrightarrow \left[\begin{matrix} CO \\ N\dot{B}r \\ CO \end{matrix} Br \right] \xrightarrow{RH}$$

$$SH + RBr + Br\cdot (or +R\cdot + Br_2) \quad (15)$$

the same problem arises in chlorinations involving $ArICl_2$ (or $ArI + Cl_2$)[35] where an intermediate $Ar\dot{I}Cl$ is believed to be involved, and the localization of the odd electron on or near the I atom is clearly shown by Breslow's elegant regioselective intramolecular chlorinations on steroids to which suitable aryl iodides have been attached.[36]

In summary, both product distributions and kinetic studies of NBS brominations in the presence of DCE and Br_2 appear incompatible with simple competing succinimide radical and bromine atom chains. Our kinetic results indicate that, in the presence of DCE, the rate-controlling step is predominantly ring opening of a succinimide radical (S·) which competes favorably with S· attack on solvent. In the presence of Br_2, the rate-determining step is attack of some chain-carrying radical on solvent (CH_2Cl_2). Both processes are quite slow, although faster than reactions of Br· generated from Br_2 alone. These results, particularly the low reactivity of S· together with its required long life, make it unlikely that it is an electronically excited species or that the chain carrier in the presence of Br_2 is the ground-state succinimide radical.

Our kinetic results are preliminary, and the work is being continued, but it seemed desirable to report them at this time, lest the interpretation of these reactions in terms of $S_\sigma\cdot$ and $S_\pi\cdot$ radicals be too uncritically accepted. We suggest that the chain carrier in NBS–Br_2 is neither a succinimide radical nor a simple bromine atom, but some third species derived from NBS and Br· and hope that additional work will identify it more definitely. In particular, since the rates of reaction of both of the radicals involved appear to be slow, one might expect that they could be identified by ESR or fast spectroscopic techniques. As far as we know, this has not been accomplished in solution approaching reaction conditions,[37] although the ESR spectra of the succinimide radical in irradiated NBS crystals at 26 K has recently been reported,[38] and it has been shown to have the expected π radical structure.

Experimental Section

Materials were commercial reagents, purity checked by spectra or GLC analysis. NBS and benzoyl peroxide were recrystallized material, purity checked by iodometric titration. For kinetic experiments DCE was fractionally distilled to remove any possible inhibitors, although this was found to have no effect on product distributions.

Reactions were carried out either on 2–5 mL samples in screw-cap vials or, more frequently, on 0.5-mL samples in stoppered NMR tubes. Materials were weighed into the tubes, and the tubes chilled to –78 °C and O_2 flushed out by bubbling with argon or N_2. Removal of O_2 effectively eliminated induction periods in kinetic runs but had no significant effect on product distributions.

After sample preparation, the tubes were placed in thermostated baths for times indicated in the Tables. For UV photoinitiated reactions irradiation was performed using a 450 watt Hanovia immersion lamp at a distance of 10 cm. For visible light initiation, 660-w incandescent lamp was used at approximately 20 cm.

Kinetic runs were followed by taking NMR spectra at suitable intervals, and, in the thermally initiated runs, the samples were carefully shielded from light. Some plots of actual data are shown in Figure 1.

Product Analyses. Major reaction products have been well characterized previously. Relative yields of $CHCl_2Br$ and neopentyl bromide for calculation of r's were determined by GLC analysis, calibrated with authentic materials. Unreacted Br_2 and NBS were destroyed by shaking with $NaHSO_3$ solution, toluene was added as an internal standard, and analysis was carried out on 20% SE-30 columns at 60 °C. While NBS–DCE–CH_2Cl_2 reactions gave significant yields of $CHCl_2Br$, NBS–DCE–CH_2Cl_2–neopentane reactions gave neopentyl bromide but only negligible traces of $CHCl_2Br$ corresponding to $r \gg 20$. We have no explanation of this discrepancy with previous reports but note that our samples of CH_2Cl_2 all contained a small amount of impurity with a GLC peak close to, but clearly resolved from, $CHCl_2Br$ (as demonstrated by adding authentic $CHCl_2Br$).

In addition to the experiments in Table I, r's for Br_2 reactions (visible light, 50 °C) were also determined in the presence of a number of other carbonyl compounds: CCl_3COCCl_3, benzophenone, benzil, phenyl benzoate, phenylglyoxalic acid, phthalic anhydride, anthraquinone, succinic anhydride, trifluoroacetophenone, and CH_3COCF_3, all approximately 1 M. All experiments gave r's = 0.1–0.4, with no obvious correlation with additive structure.

Other major products were monitored by proton NMR (Model EM-390 90 MHz Varian instrument), using the following peaks: NBS, δ 3.0 (s, 4 H); succinimide, δ 2.8 (s, 4 H); BPI, δ 3.20 (t, 2 H); 3.70 (t, 2 H); $CHCl_2Br$, δ 7.3 (s, 1 H); neopentyl bromide, δ 3.30 (s, 2 H); AIBN, δ 1.88 (s, 12 H); α-bromoisobutyronitrile, δ 2.25 (s, 6 H). Experiments in the presence of higher concentrations of DCE showed, in addition, peaks at δ 2.9 (s, 4 H) and 3.85 (s, 2 H) tentatively identified as the NBS–DCE addition product, *N*-(2-bromo-2,2-dichloroethyl)succinimide. The presence of BPI was further verified by its strong, characteristic IR absorption at 2245 cm^{-1}; when it was present in only small quantities, yields (under 15%) were estimated from the intensity of this peak, calibrated against higher yield runs which could be determined accurately by NMR.

Material balances for succinimide derivatives, NBS, succinimide, BPI, and addition product were determined on many experiments and were essentially quantitative (100 ± 3%). However, succinimide yields were commonly a few percent higher than $CHCl_2Br$ + neopentyl bromide, indicating some NBS loss by additional unidentified reactions.

Kinetic Isotope Effects. A reaction mixture of 0.14 mmol of NBS, 7.713 mmol of CD_2Cl_2, 1.478 mmol of CH_2Cl_2, and 0.44 mmol of Br_2 was irradiated at 15 °C and analyzed by GLC–MS. The most prominent peaks in the spectra of the $CH(D)Cl_2Br$ product were for the $CH(D)Cl_2^+$ ion at m/e 83 and 84, ratio 100:62.5. After the small m/e 84 peak from reference $CHCl_2Br$ was corrected for (83:84 ratio = 100:13), these data gave $k_H/k_D = 10.54$. As a check, yields of $CHCl_2Br$ and $CDCl_2Br$ were determined by GLC (which counts both) and proton NMR (which counts only $CHCl_2Br$). Two determinations gave $k_H/k_D = 9.63$ and 10.4. In a second reaction 0.124 mmol of NBS, 6.026 mmol of $CDCl_2$, 1.537 mmol of CH_2Cl_2, and 0.005 mmol of DCE were irradiated and analyzed, m/e 83:84, corrected as above, ratio 100:37, giving $k_H/k_D = 10.59$. GLC analysis indicated 0.0352 mmol of $CH(D)Cl_2Br$ while NMR integration gave 0.0253 mmol of $CHCl_2Br$. These data indicate $k_H/k_D = 10.02$. the numbers from the GLC-MS measurements are more direct and considered more accurate.

(35) Russell, G. A. *J. Am. Chem. Soc.* **1958**, *80*, 4987. Banks, D. F.; Huyser, E. S.; Kleinberg, J. *J. Org. Chem.* **1964**, *24*, 3692. Tanner, D. D.; Van Bostelen, P. B. *Ibid.* **1967**, *32*, 1517–1521.

(36) Breslow, R.; Corcoran, R. J.; Snider, B. B.; Doll, R. J. Khanna, P. L.; Kaleya, R. *J. Am. Chem. Soc.* **1977**, *99*, 905–915.

(37) UV photolysis of NBS in CH_2Cl_2 in a flow ESR system which gives excellent spectra of amidyl and many other radicals gives no detectable spectra, Ingold, K. U., private communication. This may indicate that NBS photolysis yields BPI directly as the major product, cf. Table III and our previous discussion.

(38) Lund, A.; Samskog, P. O.; Eberson, L.; Lunell, S. *J. Phys. Chem.* **1982**, *85*, 2458.