

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

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

Appendix

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

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

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

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

Similarly, to obtain the yield of BPI, Y

$$\frac{d[BPI]/dt}{d[\text{total products}]/dt} = \frac{k_5[S\cdot]}{(k_1[A] + k_3[B] + k_5)[S\cdot] + (k_2[A] + k_4[B])[X\cdot]} \quad (13)$$

Integrating

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

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

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

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Registry No. NBS, 128-08-5; BPI, 18926-24-4; NSH, 123-56-8; NIS, 516-12-1; IPI, 82621-86-1; CH₂Cl₂, 75-09-2; C₂H₄Br₂, 106-93-4; CHCl₂Br, 75-27-4; C₃H₁₁Br, 630-17-1; Br₂, 7726-95-6; I₂, 7553-56-2; CHCl₂I, 594-04-7; C₃H₁₁I, 15501-33-4; C₂H₄, 74-85-1; neopentane, 463-82-1.

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

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Abstract: The NBS brominations of methylene chloride with added substrates which yield stable radicals were reinvestigated. The proposal that these substrates would affect the ratio of β -bromopropionyl isocyanate (BPI)/bromodichloromethane, the solvent bromination product, was not substantiated. Bromination of 2,3-dimethylbutane, cyclohexene, and butadiene by NBS in CH₂Cl₂ plus vinylidene chloride gives essentially the same BPI/CHCl₂Br ratios as in the presence of neopentane but large yields of brominated and polybrominated products. Similar reactions in the presence of up to 2.5 M benzene always yield BPI but also highly brominated benzene derivatives. BPI is detected in the NBS bromination of chloroform under all conditions and is the major product in the presence of vinylidene chloride. Photolysis of *N*-iodosuccinimide-I₂ in CHCl₃ gives β -iodopropionyl isocyanate as the chief product. None of these observations support the hypothesis of σ and π states of the succinimidyl radical, while the NBS results appear consistent with competing S \cdot -Br \cdot chains.

In a series of papers starting in 1978³ Skell has proposed that radical chain brominations by *N*-bromosuccinimide (NBS) may proceed through two different succinimidyl radicals, an excited S \cdot generated by the exothermic reaction of reactive primary and secondary radicals with NBS, and a ground-state S \cdot from the reaction of allylic radicals, CCl₃ \cdot and Br \cdot with NBS (tertiary

radicals were proposed to give both S \cdot and S \cdot). These S \cdot and S \cdot radicals show different selectivities (r 's) for pairs of substrates, and only S \cdot undergoes ring opening to yield β -bromopropionyl isocyanate (BPI). The strongest evidence for Skell's proposal has come from his data on product distributions in the NBS-CH₂Cl₂-neopentane system. However, in the preceding paper,⁴ we have shown that, when the products formed in this system are reexamined by what we believe to be a more reliable analytical method (high-field NMR, supplemented by GC analysis), most of the results are consistent with simple competing succinimidyl radical (S \cdot , equivalent in properties to Skell's S \cdot) and bromine atoms as the chain carrying species. The mixed chain, S \cdot and Br \cdot , has been shown previously to control the reactions of the more reactive substrates cyclohexane and cyclopentane.⁵

(1) Presented in part at the Fourth International Symposium on Organic Free Radicals, St. Andrews, Scotland, July 10, 1984.

(2) Taken in part from: Meintzer, C. P. Ph.D. Dissertation, University of Alberta, 1984.

(3) (a) Day, J. C.; Kasaros, M. G.; Kocher, W. D.; Scott, G. E.; Skell, P. S. *J. Am. Chem. Soc.* **1978**, *100*, 1950. (b) Skell, P. S.; Day, J. C. *J. Am. Chem. Soc.* **1978**, *100*, 1951. (c) Tlumak, R. L.; Day, J. C.; Slanga, J. P.; Skell, P. S. *J. Am. Chem. Soc.* **1982**, *104*, 7257. (d) Tlumak, R. L.; Skell, P. S. *J. Am. Chem. Soc.* **1982**, *104*, 7267. (e) Skell, P. S.; Tlumak, R. L.; Seshadri, S. *J. Am. Chem. Soc.* **1983**, *105*, 5125. (f) Skell, P. S. *J. Am. Chem. Soc.* **1984**, *106*, 1838. (g) Skell, P. S.; Seshadri, S. *J. Org. Chem.* **1984**, *49*, 1650.

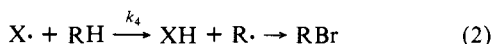
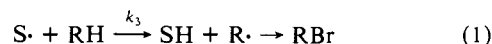
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Table I. The Photobromination of a Graded Series of Substrates with NBS-Vinylidene Chloride^a in Dichloromethane, 15 °C

substrates, ^a	products	amount, mmol		
				lit. ^{3d}
CH ₂ Cl ₂ (15.0)	% reaction	20-49	85-87	100
neo-C ₅ H ₁₂ (0.38)	BPI	(0.14 ± 0.09)	(0.40 ± 0.01)	(1.58)
CH ₂ CCl ₂ (0.074)	BrCHCl ₂	(0.0031 ± 0.0011)	(0.012 ± 0.0006)	(0.033)
	C ₅ H ₁₀ Br	(0.010 ± 0.004)	(0.033 ± 0.001)	(90.041)
	succinimide	(0.11 ± 0.02)	(0.13 ± 0.01)	(0.075)
	BrCH ₂ CCl ₂ Br	(0.0016 ± 0.0006)	(0.0067 ± 0.0004)	(n.d.)
	CHCl ₂ Br/BPI	0.022 ± 0.012	0.031 ± 0.003	0.021
CH ₂ Cl ₂ (15.0)	% reaction	24-58	100	100
cyclopentane (0.38)	BPI	(0.10 ± 0.06)	(0.29 ± 0.02)	(1.41)
CH ₂ CCl ₂ (0.076)	BrCHCl ₂	(0.0025 ± 0.0009)	((8.1 ± 0.4) × 10 ⁻³)	(0.035)
	C ₅ H ₉ Br	(0.039 ± 0.02)	(0.24 ± 0.03)	(0.25)
	succinimide	(0.13 ± 0.03)	(0.30 ± 0.03)	(0.275)
	BrCH ₂ CCl ₂ Br	((2.0 ± 1.0) × 10 ⁻⁴)	(0.015 ± 0.001)	(n.d.)
	CHCl ₂ Br/BPI	0.025 ± 0.005	0.028 ± 0.002	0.025
CH ₂ Cl ₂ (15.0)	% reaction	45-56	100	100
2,3-dimethyl-	BPI	(0.17 ± 0.03)	(0.28 ± 0.02)	(1.25)
butane (0.38)	BrCHCl ₂	(0.0044 ± 0.0006)	(0.010 ± 0.001)	(0.056)
CH ₂ CCl ₂ (0.071)	1-Br-C ₆ H ₁₃	(0.0032 ± 0.0003)	(0.0059 ± 0.0001)	(0.079)
	2-Br-C ₆ H ₁₃	(0.014 ± 0.001)	(0.013 ± 0.004)	(0.21)
	2,3-Br ₂ -C ₆ H ₁₂	(0.0056 ± 0.0013)	(0.013 ± 0.001)	(n.d.)
	2,3-dimethyl-2-butene	n.d. ^c	(0.0011 ± 0.0005)	(n.d.)
	succinimide	(0.18 ± 0.04)	(0.31 ± 0.002)	(0.35)
	BrCH ₂ CCl ₂ Br	(0.0050 ± 0.0013)	(0.034 ± 0.003)	(n.d.)
	CHCl ₂ Br/BPI	0.024 ± 0.005	0.035 ± 0.001	0.045
CH ₂ Cl ₂ (15.0)	% reaction	41-53	100	>93
cyclohexene (0.38)	BPI	(0.012 ± 0.003)	(0.036 ± 0.016)	(0.62)
CH ₂ CCl ₂ (0.085)	BrCHCl ₂	((5.1 ± 0.1) × 10 ⁻⁴)	((7.6 ± 0.3) × 10 ⁻⁴)	(0.045)
	4-Br-C ₆ H ₉	(0.0044 ± 0.0006)	(0.0048 ± 0.0001)	(0.022)
	3-Br-C ₆ H ₉	(0.032 ± 0.004)	(0.019 ± 0.005)	(0.110)
	1-bromo-2-succinimidylbenzene	(0.074 ± 0.001)	(0.15 ± 0.01)	(0.77)
	benzene	((8.56 ± 2.34) × 10 ⁻⁴)	(0.010 ± 0.0008)	(n.d.)
	1,3-cyclohexadiene	(0.0033 ± 0.0009)	(0.020 ± 0.007)	(n.d.)
	1,2-Br ₂ -C ₆ H ₁₀	(0.090 ± 0.005)	(0.19 ± 0.02)	(n.d.)
	succinimide	(0.22 ± 0.002)	(0.39 ± 0.004)	(0.18)
	CHCl ₂ Br/BPI	0.043 ± 0.008	0.023 ± 0.034	0.073
CH ₂ Cl ₂ (15.0)	% reaction	41-44	100	n.r. ^d
1,3-butadiene (0.36)	BPI	n.d. ^c	(0.15 ± 5 × 10 ⁻⁴)	(n.d.)
CH ₂ CCl ₂ (0.073)	BrCHCl ₂	n.d.	(0.0063 ± 2 × 10 ⁻⁴)	(0.029)
	NS-CH ₂ -CH=CH-CH ₂ -Br	(0.038 ± 0.003)	(0.51 ± 0.002)	(0.95)
	NS-CH ₂ -CHBr-CH=CH ₂			
	BrCH ₂ -CH=CH-CH ₂ Br	(0.054 ± 0.004)	(0.08 ± 5 × 10 ⁻⁴)	(n.r.)
	succinimide	(0.066 ± 0.007)	(0.12 ± 0.001)	(n.r.)
	CHCl ₂ Br/BPI		0.043 ± 0.001	

^aReaction conditions taken from ref 3d (0.68 mmol of NBS in 2 mL of CH₂Cl₂). ^bStructure tentatively assigned, see Experimental Section. ^cn.d. = product not detected. ^dn.r. = not reported.

In any system where S· and another radical X· (which does not yield BPI) compete for a substrate RH, relative yields of RBr and BPI are determined by the competing reactions



and it is clear that any intrusion of X· into the reaction will increase the RBr/BPI ratio in the products. It should be noted that if X· is relatively unreactive toward RH, but reacts readily with other substrates in the system, it can still make a significant contribution to total products without appreciably changing the RBr/BPI ratio. This will be important in our later discussion.

Skell^{3d} has applied this criterion to a "graded series" of substrates RH in CH₂Cl₂ in which R·'s would be expected to give increasing quantities of S_π· radicals by reaction with NBS, by examining the ratios of CHCl₂Br/BPI in the products, and has

reported results consistent with his scheme. In this paper we report a reexamination of several of his systems in which we apply the analytical methods of our preceding papers^{4,5} to products.

Results and Discussion

The Graded Series. We have reexamined several examples of Skell's "graded series", using his concentrations of reactants which included vinylidene chloride to scavenge adventitious Br· radicals, in order to reexamine his criterion of CHCl₂Br/BPI yields. Results at low and high NBS conversions are shown in Table I and are compared to the previous results. The first observation is that CHCl₂Br/BPI ratios vary much less than reported and, in fact, hardly differ significantly from values with RH-neopentane, a system which all investigators agree involves essentially pure S· chains under these conditions.

Second, with some substrates we find products which have not been reported previously and which bear upon the nature of the chain carrying radicals involved. Thus, with 2,3-dimethylbutane (DMB) at high conversion, previously unreported 2,3-Br₂-DMB is a major product of DMB reaction. Since 2-Br-DMB is well known to be much more reactive toward Br· than DMB,⁶ we

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Table II. The Photobromination of Dichloromethane with NBS-Vinylidene Chloride with Added Benzene, 15 °C

substrates, ^a M		products	amounts, mmol		lit. ^{3d}
CH ₂ Cl ₂ (15.0) benzene (0.40) CH ₂ CCl ₂ (0.085)	% reaction		27-46	100	n.r. ^b
	BPI		(0.062 ± 0.017)	(0.16 ± 0.002)	0.34
	BrCHCl ₂		(0.015 ± 0.004)	(0.11 ± 0.015)	0.10
	<i>N</i> -phenylsuccinimide		(0.026 ± 0.005)	(0.051 ± 0.003)	0.14
	succinimide		(0.14 ± 0.02)	(0.38 ± 0.054)	0.31
	BrCH ₂ CCl ₂ Br		(0.013 ± 0.002)	(0.015 ± 4 × 10 ⁻⁴)	0.14
	6-succinimidyl-3,4,5-tribromocyclohexene ^b CHCl ₂ Br/BPI		(0.004 ± 0.004)	(0.046 ± 0.011)	n.d. ^c
		0.240 ± 0.090	0.685 ± 0.087	0.294	
CH ₂ Cl ₂ (12.1) benzene (2.55) CH ₂ CCl ₂ (0.088)	% reaction		39-47	100	n.r.
	BPI		(0.048 ± 0.001)	(0.073)	n.d.
	BrCHCl ₂		(0.014 ± 0.003)	(0.026)	0.20
	<i>N</i> -phenylsuccinimide		(0.055 ± 0.004)	(0.070)	0.34
	succinimide		(0.192 ± 0.008)	(0.258)	0.12
	BrCH ₂ CCl ₂ Br		(0.02 ± 0.007)	(0.025)	0.33 ^d
	6-succinimidyl-3,4,5-tribromocyclohexene CHCl ₂ Br/BPI		(0.0055 ± 0.00009)	(0.203)	n.d.
		0.292 ± 0.028	0.361		

^a Reaction conditions taken from ref 3d (0.68 mmol of NBS in 2 mL of CH₂Cl₂). ^b n.r. = not reported. ^c n.d. = not detected. ^d Olefin used was 3,3-dimethyl-1-butene, and the value given for the dibromide was for 1,2-dibromo-3,3-dimethylbutane.

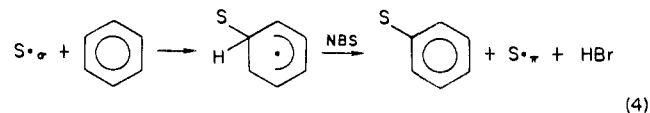
consider this (as well as the formation of significant amounts of CH₂BrCCl₂Br from the vinylidene chloride present) strong evidence for Br· participation in the total reaction. However, since the tertiary hydrogens of DMB are some 2500 times as reactive as CH₂Cl₂ toward Br·,⁷ the actual [Br·]/[S·] ratio in the system could still be very low, and we see that the CHCl₂Br/BPI ratio is hardly increased.

Cyclohexene results are similar in that 1,2-dibromocyclohexane (again previously unreported) actually accounts for almost half of the cyclohexene derived products. We again take this as evidence for Br· participation, and if we are dealing with simply competing S· and Br· chains the latter accounts for most of the total products. Cyclohexene is evidently a good trap for both radicals, and the rate constant for S· addition appears to be 0.15/(0.036 × 0.38) = 11 times that for ring opening.

Finally, our results with butadiene again show that dibromide makes up 14% of the butadiene reacted. We would say that butadiene traps both Br· and S· with a rate constant for addition again about 11 times that for ring opening, if we assume that the [butadiene] is essentially constant (0.59/0.15 × [butadiene]_{av}).

Since there appears to be a large Br· component in all the reactions involving tertiary and allylic C-H bonds, there is no good way of sorting out the relative reactivities of such substrates to S· radicals.

Benzene. Skell has shown that S· radicals add readily to benzene to give *N*-phenylsuccinimide (plus other products) and has proposed that the resulting bromocyclohexadienyl radicals react with NBS to yield S_π·, since he detected no BPI in the presence of >2 M benzene. The HBr reacts with more NBS to yield Br₂, but



whether an intermediate cyclohexadiene product is formed which rapidly loses HBr is not clear. In the presence of vinylidene chloride or other olefins the Br₂ is rapidly taken up, leading to similar yields of *N*-phenylsuccinimide and addition product. Our own results on the effect of benzene on NBS brominations in the presence of vinylidene chloride as a Br· trap appear in Table II. Although we also find large CHCl₂Br/BPI ratios indicating the importance of some other X· radical, our data otherwise differ significantly from Skell's findings.

First, BPI is found at all benzene concentrations (see Experimental Section), and the yield in 2.5 M benzene is comparable to that of *N*-phenylsuccinimide. Second, additional products, including one tentatively identified as 6-succinimidyl-3,4,5-tri-

(7) The preceding paper⁴ gives a more detailed discussion of these relative rates.

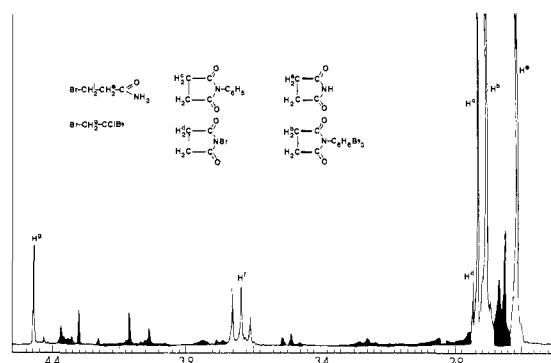


Figure 1. The FT ¹H 200 MHz NMR spectrum (48 scans) of the nonvolatile reaction products from the NBS photobromination of methylene chloride with added benzene (2.55 M) and vinylidene chloride. Shaded area are unidentified products.

bromocyclohexene (see Experimental Section) are present. Basically, *N*-phenylsuccinimide yields are low, and the reactions are messy. Figure 1 shows a typical NMR spectrum of a reaction mixture (after removal of CH₂Cl₂, benzene, and volatile products).

Identified peaks are indicated, but it is clear that many other products are present. In our view, the presence of BPI and highly brominated products are most consistent with S· and Br· chains, but the reactions are too indiscriminate for detailed analysis of reaction paths. Comparison of BPI and *N*-phenylsuccinimide yields indicate that the rate of S· addition to the benzene ring is 1-2 times that for ring opening.

Chloroform. A repeated tenet of the S_σ·-S_π· scheme has been that CCl₃· reacts with NBS to give S_π·.^{1d,e} Accordingly, a simple reaction scheme predicts that NBS brominations in CHCl₃ should give CCl₃Br and no BPI even in the presence of Br· traps. The actual facts are considerably more complicated. The BPI forming reaction was first discovered in CHCl₃ containing a little allyl chloride^{8a} and independently in 1,4-endocyclohexane,^{8b} and Skell reports good yields in the presence of *tert*-butylethylene.^{3d} It is only in the presence of vinylidene chloride as the Br· trap that it is claimed that no BPI is formed, and here contrary results have been reported by Walling.^{9,10} Our experiments are shown in Table III, and we think they need little discussion. BPI is detected under all conditions (including in the presence of added Br₂), and yields

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(b) Martin, J. C.; Bartlett, P. D. *J. Am. Chem. Soc.* **1957**, *79*, 2533.

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(10) A similar observation was reported by Skell with no BPI detected by his analytical technique until the vinylidene chloride present had been consumed.

Table III. The Photobromination of Chloroform (12.4 M) with NBS and Additives, 15 °C

additive [M]	[NBS]	reaction, ^a %	yield of products, ^{a,b} %					mass balance, %	
			CCl ₃ Br	BrCH ₂ C- Cl ₂ Br	C ₂ Cl ₆	β -BPIC	NSH	NS-	Br-
none	0.099	100	85.5		0	19.8	80.2	100	105
DPBO ^c (0.0052)	0.074	49-63	69.8 \pm 5.9		4.2 \pm 1.9	10.5 \pm 2.7	89.4 \pm 2.7	100 \pm 0.3	80.3 \pm 6.1
bromine (0.0011)	0.096	100	101		0	2.31	97.7	100	103
vinylidene chloride (0.063)	0.096	100	0.43 \pm 0.07	2.2 \pm 0.3	0	82.7 \pm 1.5	17.4 \pm 1.4	100	87.5 \pm 0.4
vinylidene chloride (0.071)	0.34	22-35	n.d. ^d	1.9 \pm 0.8	n.d.	40.8 \pm 5.1	55.0 \pm 2.0	97.7 \pm 4.9	44.6 \pm 5.9
vinylidene chloride (0.071)	0.34	100	3.4 \pm 0.4	3.0 \pm 1.0	0.05 \pm 0.02	74.0 \pm 1.0	18.0 \pm 2.0	92.0 \pm 3.0	82.3 \pm 3.2

^aBased on the amount of NBS consumed. ^bThe errors reported are the average deviation from the mean value of three more independent experiments. ^cThe reaction was carried out in the absence of light with added di-*tert*-butyl peroxyoxalate, DBPO. The values reported are the average of three independent experiments. ^dn.d. = not detected.

Table IV. The Photoiodination of Chloroform with NIS-I₂, 15 °C

reagent, M [NIS]/[I ₂]	reaction, ^a %	yield of products, ^a %			
		CCl ₃ I	C ₂ Cl ₆	IPI	NSH
0.017/0.011	100	2.63	0.218	75.3	24.7
0.024/0.0026	100	1.37	0.232	69.2	30.8
0.15 ^b /5.8 \times 10 ⁻³	11.0	44.2	0.97	44.5	67.8
0.15 ^b /5.8 \times 10 ⁻³	14.2	34.5	1.88	48.6	48.4

^aBased on the amount of NIS consumed. ^bThe NIS used exceeded its soluble concentration.

of high conversion experiments in the presence of vinylidene chloride are close to Walling's findings. The high yields of BPI imply essentially pure S \cdot chains with no evidence for an S \cdot species. The only peculiarity in the data is the poor material balance for bromine in low conversion experiments in the presence of vinylidene chloride. We suspect that CCl₃ radicals are being consumed by addition to olefin.

In support of the S \cdot -S \cdot scheme, it has also been claimed that *N*-iodosuccinimide (NIS)-I₂ halogenations give the same r values as NBS-Br₂ reactions and no β -iodopropionyl isocyanate (IPI).^{3c} In the preceding paper, we showed that the isocyanate is actually formed in high yield in CH₂Cl₂. Table IV shows that this is also true in CHCl₃, so NIS-I₂ reactions again in our hands give no support to a S \cdot -S \cdot formulation.

Summary

1. From our data, CHCl₃Br/BPI ratios in NBS-CH₂Cl₂-C-H₂CCl₂ reactions are essentially the same in the presence of DMB, cyclohexene, and butadiene as in the presence of neopentane. This is contrary to the results reported by Skell^{3d} where the ratios reported appear to be the results of faulty analysis and incorrect identification of products. 2. On the other hand, most of the NBS is actually consumed by reaction with these substrates, and the formation of significant amounts of polybrominated products is consistent with the participation of Br \cdot chains. 3. Reactions in the presence of even 2.5 M benzene yield BPI as well as *N*-phenylsuccinimide. Polybrominated products are again produced, consistent with Br \cdot chains, but the reactions are messy, give a variety of unidentified products, and are not really susceptible to detailed interpretation. BPI, polybrominated products, and unidentified materials (which make up the majority of the reaction products) were not found previously^{3d} and constitute the basis for the reinterpretation of the significance of the previous interpretation. 4. The NBS bromination of chloroform in the absence of oxygen gives BPI under all conditions and high yields in the presence of vinylidene chloride, confirming Walling's conclusions.⁹ This is contrary to Skell's previous report^{3c} and his suggestions that Walling's results were due to the presence of oxygen. 5. Photolysis of *N*-iodosuccinimide-I₂ in chloroform gives β -iodopropionyl isocyanate as the major product. This observation constitutes a new piece of evidence contrary to the formation of a π radical. 6. None of these results provide evidence for two states of the succinimidyl radical in preference to simple competing S \cdot and Br \cdot chains.

Experimental Section

Materials. The source, purity, and handling of the materials neopentane, bromine, iodine, *N*-bromosuccinimide, *N*-iodosuccinimide, 1,1-

dichloroethene, and methylene chloride are the same as those given in the previous manuscript.⁴

Cyclopentane (Phillips 66, research grade) was heated to reflux over P₂O₅ and fractionally distilled with use of an 18-in. Vigreux column. The middle fractions were collected. GLC analysis showed them to be >99.9% pure.

Benzene (American Chemicals Ltd.) was dried over sodium wire and distilled prior to use. GLC analysis showed it to be >99.9%.

Chloroform (American Chemicals Ltd.) was distilled through a 3-ft Teflon spinning-band column. It was further distilled from P₂O₅ through an 18-in. Vigreux column immediately prior to use. GLC analysis showed it to be >99.98%.

Cyclohexene (BDH) was dried over sodium sulfate and filtered and distilled through a 3-ft stainless steel spinning-band column. GLC analysis showed it to be 99.8%. Impurities were identified as benzene (0.13%) and 1,3-cyclohexadiene (0.07%) by a comparison of their GLC retention times and mass spectral cracking patterns (GC/MS).

1,3-Butadiene (Matheson, research grade >99.9%) was distilled prior to use. In several samples of butadiene (Matheson Research grade >99.9%) small amounts of two unidentified impurities are detectable by ¹H NMR analysis (δ 7.335 and 7.325). Only by high-resolution NMR analysis would these products be obviously differentiated from bromodichloromethane, δ 7.25, and then only if one was aware of the problem.

2,3-Dimethylbutane (Phillips 66, research grade >99.88%) was used without further purification.

Di-*tert*-butyl peroxyoxalate was prepared from *tert*-butyl hydroperoxide and oxalyl chloride with use of the procedure of Bartlett.¹¹ The white needles obtained were stored in the dark at -20 °C until used.

Iodotrichloromethane was prepared from trichloroacetyl chloride and hydrogen iodide following the procedure of Simons, Sloat, and Meunier.¹² The colorless liquid product was stored in the dark since it rapidly turned a color characteristic of iodine upon exposure to room light: bp 124-126 °C (690 mm) [lit.¹³ bp 140-142 °C (760 mm)]; 80 MHz ¹H NMR (CD₃CN) no peaks; IR 745 (s), 680 cm⁻¹ (m).

β -Bromopropionamide was prepared from β -bromopropionic acid by heating to reflux with PCl₃ to yield the acid chloride, followed by reaction with ammonium hydroxide.¹⁴ The precipitated product was washed three times with ice-cold water and dried: mp 110-113 °C [lit.¹⁵ mp 111 °C]; 80 MHz ¹H NMR (CDCl₃) δ 2.75 (t, J = 7 Hz, 2 H), 3.61 (t, J = 7 Hz, 2 H), 6.20 (br s, 2 H).

β -Iodopropionamide was prepared from β -iodopropionic acid by heating to reflux with PCl₃ to yield the acid chloride, followed by reaction with ammonium hydroxide.¹⁴ The product was dried by suction and recrystallized from acetonitrile: mp 135-136 °C dec [lit.¹⁶ mp 140.5 °C]; 80 MHz ¹H NMR (CDCl₃) δ 2.86 (t, J = 6.9 Hz, 2 H), 3.37 (t, J = 6.9 Hz, 2 H), 5.66 (br s, 2 H); mass spectrum m/e (rel intensity) 199 (29.1), 127 (12.9), 72 (98.2), 55 (7.8), 44 (100), 28 (16.4). Anal. Calcd for C₃H₆INO: C, 18.11; H, 3.04. Found: C, 18.15; H, 3.03.

3-Bromocyclohexene was prepared by heating cyclohexene and NBS to reflux to carbon tetrachloride. The organic layer was washed with aqueous sodium thiosulfate solution and water and then dried over sodium sulfate. The colorless liquid product was obtained by fractional distillation: bp 84-86 °C (42 mm) [lit.¹⁷ bp 80-82 °C (40 mm)].

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4-Bromocyclohexene was prepared from 1,4-cyclohexanediol and PBr_3 according to the procedure of Fish and Broline:¹⁸ bp 62 °C (21 mm) [lit.¹⁸ bp 50–52 °C (22 mm)].

N-Phenylsuccinimide was prepared from succinic anhydride and aniline following the procedure of Cava, Deana, Muth, and Mitchell.¹⁹ The white needles obtained were recrystallized from 98% ethanol: mp 153–154 °C [lit.²⁰ mp 150–152 °C]; 200 MHz ^1H NMR (CD_3CN) δ 2.91 (s, 4 H), 7.45 (m, 5 H).

1-Bromo-2-succinimidylcyclohexane was isolated from a reaction of cyclohexane with NBS by extraction of the nonvolatile products with CCl_4 as a colorless liquid: 200 MHz ^1H NMR (CDCl_3) δ 1.19–2.23 (m, 8 H), 2.72 (s, 4 H), 4.13 (m, 1 H), 4.83 (m, 1 H) [lit.²⁰ 60 MHz δ 1.15–2.1 (m, 8 H), 2.7 (s, 4 H), 3.8–5.0 (m, 2 H)]; mass spectrum m/e (rel intensity) 261 (1.6), 259 (1.7), 180 (2.0), 100 (100).

6-Succinimidyl-3,4,5-tribromocyclohexene was isolated from a reaction of benzene with NBS as described by Chow.²¹ The white solid was separated by column chromatography on alumina with $\text{CCl}_4/\text{CH}_2\text{Cl}_2$: mp 194–204 °C dec [lit.²⁰ mp 204–207 °C]; Fourier transform IR 1700, 1190, 1160, 740 cm^{-1} [lit.²⁰ PE 457 grating spectrometer IR 1700, 1185, 1165, 780 cm^{-1}]; 200 MHz ^1H NMR (CDCl_3) δ 2.88 (s, 4 H), 4.65–5.24 (m, 3 H), 5.24–5.80 (m, 3 H) [lit.²⁰ 60 MHz NMR 2.86 (s, 4 H), 4.8–5.17 (m, 3 H), 5.34–5.62 (m, 1 H), 6.00 (m, 2 H)]; mass spectrum m/e (rel intensity) 419 (0.2), 417 (0.7), 415 (0.8), 413 (0.4), 336 (7.6), 334 (15.1), 332 (8.1), 100 (100) [lit.²⁰ mass spectrum m/e (rel intensity) 419 (0.2), 417 (0.5), 415 (0.5), 413 (0.2)]. Exact mass calcd for $\text{C}_{10}\text{H}_8\text{NBr}_2\text{O}_2$: 335.88814, 333.89014, 331.89214. Found: 335.8879, 333.8895, 331.8911.

1,3-Butadiene Addition Products. The addition products resulting from the experiments with 1,3-butadiene present were isolated by chromatographing the product mixture on alumina (chloroform–methanol).

1-Bromo-4-succinimidyl-2-butene: ^1H NMR (CDCl_3) δ 2.64 (s, 4 H), 3.2–4.4 (m, 4 H), 5.3–5.9 (m, 2 H) [lit.^{3d} ^1H NMR (CDCl_3) δ 2.7 (s, 4 H), 3.3–4.4 (m, 4 H), 5.5–5.9 (m, 2 H)]. **3-Bromo-4-succinimidyl-2-butene:** ^1H NMR (CDCl_3) δ 2.86 (s, 4 H), 3.25–3.6 (m, 2 H), 5.37–5.82 (m, 3 H), 6.27–6.51 (m, 1 H) [lit.^{3d} ^1H NMR (CDCl_3) δ 2.8 (s, 4 H), 3.3–3.7 (m, 2 H), 5.5–5.9 (m, 3 H), 6.4–6.6 (m, 1 H)].

Instrumentation. NMR spectra, 200-MHz ^1H , were obtained on a Bruker WH-200 NMR spectrometer, 80-MHz ^1H NMR spectra were obtained on a Bruker WH-80 NMR spectrometer, and 60-MHz ^1H NMR spectra were obtained on a Varian A-56/60A NMR spectrometer. GLC analyses were carried out on a Hewlett-Packard 5840A gas chromatograph equipped with a flame ionization detector and a capillary injector system. Mixtures of the authentic materials and an internal standard, all of known concentrations, were prepared and used in the GLC analysis as a calibration mixture.

The Reactions of the Graded Series with NBS in Solvent Dichloromethane. NBS and an internal standard, hexachloroethane, were weighed into Pyrex reaction ampules and aliquot samples of mixtures of dichloromethane, 1,1-dichloroethylene, and the substrate of interest were added in the absence of light. The ampules were degassed, sealed, and thermostated at 15 °C. After equilibration the reaction vessels were irradiated (20–30 h) through the Pyrex thermostat with a 400-W General Electric sun lamp.

Under the conditions reported the NBS would have been 0.34 M, but at 15 °C the mixtures were always heterogeneous. The limit of solubility of NBS in methylene chloride is approximately 0.22 M. Any added substrate only served to make the NBS less soluble; however, the reactions were carried out with use of the prescribed^{3d} recipe. The reactions were carried out so that the NBS had only partially reacted, and the solution was always at its saturation solubility. With added hydrocarbon substrates the solubility was reduced to ~ 0.1 M, and since less than a third of the NBS was soluble the reactions were carried out not only to low conversion but to 100% reaction.

After irradiation, the reaction tubes were frozen and opened and a calculated amount of water was added (just sufficient to react with the β -BPIC). If insoluble material was present, the sample was diluted with sufficient methylene chloride to dissolve the solid present. An aliquot sample was sealed in an NMR tube and analyzed by Fourier transform 200-MHz ^1H NMR for β -bromopropionamide, succinimide, and unreacted NBS. In the reactions carried out with added benzene the products *N*-phenylsuccinimide and 6-succinimidyl-3,4,5-tribromocyclo-

hexene were also quantitatively determined from the 200-MHz ^1H spectrum. In these reactions the amount of BIP formed was determined from measurement of the integration of the triplet at $\sigma = 3.61$. At the lower percentage reactions reported the triplet was clearly distinguished. At the highest percentage reactions reported the number of additional unidentified products were almost cleanly separated and an estimate of their integrated areas would be made. The remaining solution was titrated iodometrically with aqueous sodium thiosulfate. The organic phase was separated, dried, and analyzed for brominated substrates by GLC (50-m methyl silicone capillary column, 30–100 °C).

A standard mixture was prepared by using the amounts of 1,2-dibromo-1,1-dichloroethane, 1,1-dichloroethylene, and dichloromethane present at 100% reaction (in a typical experiment carried out with added benzene), and an aliquot of this mixture was irradiated in the same apparatus for an equivalent length of time as in the experiments carried out with added benzene. Comparison of the preanalyzed mixture and the reanalyzed mixture showed the 1,2-dibromo-1,1-dichloroethane to be stable to the reaction conditions ($\pm 4\%$), and no bromodichloromethane was found to have formed.

Analysis of the reactions carried out with added cyclohexene, 200-MHz FT-NMR spectra (48 scans), showed clearly that ring-opened material had been formed, but at these concentrations no bromodichloromethane (δ 7.24) could be detected. An absorption peak at δ 7.34 was observed, however, which was subsequently shown to be that of small amounts of benzene which appeared to be present in the starting cyclohexene and/or to be produced during the reaction. GLC analysis (50-m capillary column) detected the small amounts of bromodichloromethane produced by bromination and allowed an estimate of the product ratio reported.

The bromination of methylene chloride in the presence of 1,3-butadiene presented similar problems to those encountered during the NBS bromination of cyclohexene. At low conversions neither β -BPIC nor bromodichloromethane could be detected by NMR or GLC analysis. It appeared that the butadiene and 1,1-dichloroethene acted as efficient traps for both succinimidyl and bromine radicals. As was reported^{3d} previously a number of other unidentified products were also detected. At higher conversion (100%), β -BPIC could be detected by 200-MHz FT-NMR (48 scans); however, bromodichloromethane (δ 7.26) was only present in quantities which could be detected by capillary GLC analysis.

The Identification and Analysis of Benzene Produced in the Reaction with Added Cyclohexene. A solution was prepared containing cyclohexene (0.38 M) and vinylidene chloride (0.073 M) in dichloromethane. Aliquot samples were placed in NMR tubes which were protected from light; each tube contained a weighed amount of NBS. A weighed amount of bromoform, as an NMR standard, was added to one of the tubes which was sealed, analyzed by 200-MHz ^1H FT-NMR (48 scans), and found to contain benzene ($\leq 3.2 \times 10^4$ M). A second NMR tube was degassed by the freeze–thaw method (three cycles), sealed, and irradiated at 15 °C for 48 h (100% conversion of NBS). The sample was analyzed, without opening, by the same method, and benzene (δ 7.35) was detected. The NMR tube was broken open, a weighed amount of bromoform was added, the tube was resealed and analyzed by NMR once again. The sample was found to contain benzene (5.9×10^3 M; an 18-fold increase). The addition of authentic bromodichloromethane produced an additional singlet absorption in the NMR spectrum (δ 7.25).

The benzene was positively identified by comparison of its 200-MHz ^1H NMR absorption spectrum and its GLC retention time (50-m methylsilicone capillary column) with those of the authentic material. The mass spectral cracking pattern obtained through GLC–MS analysis also confirmed it as benzene.²²

The Photobromination of Chloroform with NBS. Mixtures of NBS and chloroform were placed in Pyrex reaction ampules in the absence of light. When additives, 1,1-dichloroethylene or molecular bromine, were included they were added as aliquots of standard chloroform solutions. The ampules were degassed, sealed, equilibrated at 15 °C, and irradiated as described for the reactions carried out in solvent dichloromethane.

After irradiation (~ 3 h, 100% reaction) the reaction tubes were frozen and opened, a standard, carbon tetrachloride, was added, and the solution was analyzed in a similar manner to the reactions carried out in solvent dichloromethane. The yields of succinimide and β -bromopropionamide were determined by Fourier transform 200-MHz ^1H NMR (see analysis graded series). Bromotrichloromethane and hexachloroethane were determined by GLC (50-m methyl silicone capillary column).

The Thermally Initiated Bromination of Chloroform with NBS. Mixtures of NBS, chloroform, and di-*tert*-butyl peroxyoxalate (DBPO) were placed in Pyrex reaction ampules in the absence of light. The ampules were degassed, sealed, and thermostated at 15 °C.

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After the reaction was complete, the ampules were frozen and opened. The samples were analyzed for products in the same manner as the photoinitiated samples.

The Photoiodination of Chloroform with *N*-Iodosuccinimide and Iodide. Mixtures of NIS, I₂, and chloroform were placed in Pyrex reaction ampules, in the absence of light. The ampules, were degassed, sealed, and thermostated at 15 °C. After equilibration the reaction vessels were irradiated as described for the NBS reactions.

After irradiation (6 h, 80% reaction) the reaction tubes were frozen and opened, a standard, carbon tetrabromide, was added, and a calculated amount of water was added (just sufficient to react with the β-IPIIC). An aliquot sample was sealed in an NMR tube and analyzed for succinimide and β-iodopropionamide by Fourier transform 200-MHz ¹H NMR spectroscopy. The remaining solution was titrated iodometrically with aqueous sodium thiosulfate. The organic phase was separated, dried, and analyzed for iodotrichloromethane and hexachloroethane by GLC (50-m methyl silicone capillary column).

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Registry No. NBS, 128-08-5; BPI, 18926-24-4; NIS, 516-12-1; IPI, 82621-86-1; CH₂Cl₂, 75-09-2; neo-C₅H₁₂, 463-82-1; CH₂CCl₂, 75-35-4; BrCHCl₂, 75-27-4; C₅H₁₀Br, 630-17-1; BrCH₂CCl₂Br, 75-81-0; C₅H₉Br, 137-43-9; 4-BrC₆H₅, 3540-84-9; BrCH₂CH=CHCH₂Br, 6974-12-5; CCl₃Br, 75-62-7; C₂Cl₆, 67-72-1; I₂, 7553-56-2; CCl₃I, 594-22-9; succinimide, 24344-83-0; β-bromopropionamide, 6320-96-3; β-bromopropionic acid, 590-92-1; β-iodopropionamide, 21437-81-0; β-iodopropionic acid, 141-76-4; 3-bromocyclohexene, 1521-51-3; cyclohexene, 110-83-8; 1-bromo-2-succinimidylcyclohexane, 82469-57-6; 1,3-butadiene, 106-99-0; 1-bromo-4-succinimidyl-2-butene, 82469-58-7; 3-bromo-4-succinimidyl-2-butene, 98088-05-2; succinimide, 123-56-8; cyclopentane, 287-92-3; 2,3-dimethylbutane, 79-29-8; 1-bromo-2,3-dimethylbutane, 30540-31-9; 2-bromo-2,3-dimethylbutane, 594-52-5; 2,3-dibromo-2,3-dimethylbutane, 594-81-0; 2,3-dimethyl-2-butene, 563-79-1; benzene, 71-43-2; 1,3-cyclohexadiene, 592-57-4; 1,2-dibromocyclohexane, 5401-62-7; *N*-phenylsuccinimide, 83-25-0; 6-succinimidyl-3,4,5-tribromocyclohexene, 98088-06-3; chloroform, 67-66-3; bromine, 7726-95-6.

The Electronic Structure of Selenoformaldehyde

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Abstract: Ab initio molecular orbital calculations with electron correlation were carried out to determine the electronic structures of the ground and lower excited singlet and triplet states of selenoformaldehyde (CH₂=Se). The SCF energy at the equilibrium C=Se bond length (1.739 Å) is -2438.70595 hartrees. The effect of including some electron correlation is to lengthen the bond to 1.800 Å. The lowest electronically excited state is calculated to be ³A₁ (π-π*, 1.42 eV). The second state is ³A₂ (n-π*, 1.62 eV). The next two states are ¹A₂ (n-π*, 2.02 eV) and ¹A₁ (π-π*, 4.94 eV). These valence states are followed by the singlet and triplet components of the n→5s and n→5p_z Rydberg transitions of spatial symmetry B₂ in the range 5.2-5.5 eV. Ionization potentials of CH₂=Se are estimated as 8.81 (n, 5b₂), 10.81 (π, 4b₁), 13.14 (n', 11a₁), 14.57 (4b₂), and 19.24 eV (10a₁). Calculations are also reported for thioformaldehyde.

The preparation of stable selones was first reported in 1975 by Barton and co-workers.² The chemistry and photochemistry of these species is significantly different from that of ketones. Selones have proved to be useful for the preparation of very sterically hindered molecules.^{2,3} They act as very efficient spin traps for free radicals.⁴ The photoactive state of selones appears to be the second excited singlet state rather than the first as is the case with ketones.⁵ Attempts to prepare selones result in polymeric materials unless the selenocarbonyl substituents are sterically bulky. More recently, the unstable species selenoacetaldehyde⁶ and selenoformaldehyde⁷ were prepared in the gas phase by flash pyrolysis of suitable precursors. The microwave spectrum of the former was recorded and the structure and methyl rotation barrier determined.⁶ In the case of the less stable selenoformaldehyde, the visible and near-infrared spectra were measured. The absorptions observed were identified as vibrational structure associated with the longest wavelength electronic transition, assigned as ³A₂ ← ¹A₁ (n → π*)⁷.

We report herein the results of the first ab initio investigation of the ground and electronically excited states of selenoformaldehyde using a large Gaussian basis set and with inclusion of some electron correlation.

Method

All Hartree-Fock SCF calculations were carried out with use of the GAUSSIAN 76 system of programs.⁸ For the selenium atoms, the 14s, 11p, 5d atom optimized basis set of Huzinaga^{9,10} was contracted to 8s, 5p, 2d by a Raffanetti type of contraction scheme.^{11,12} For carbon and hydrogen, the internal 6-31G split valence basis sets¹³ were employed. Single sets of diffuse s and p functions were added to Se (α_s = 0.016, α_p = 0.014) and to C (α_s = 0.02, α_p = 0.018). These functions are required to describe the lower Rydberg states of the molecule. An s-type bond function (α = 0.795) was added to the midpoint of the C=Se bond.

Post-Hartree-Fock calculations were carried out by a perturbative CI scheme which has been previously described,^{14,15} as has the method used

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