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Selectivities of π- and σ-Succinimidyl Radicals in Substitution and Addition Reactions. Appendix: Response to Walling, El-Taliawi, and Zhao

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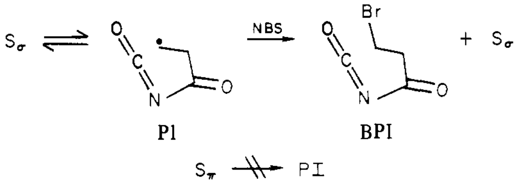
Abstract: A new method for studies of π-succinimidyl (S_π) radicals is described, one that makes possible the study of reactions of this radical with a variety of substrates not accessible by the use of Br_2–NBS. NBS systems containing $BrCCl_3$ at mole fractions greater than 0.3 show all the characteristics we have associated with S_π behavior, and they function in the presence of olefins which serve as Br_2 scavengers. If CCl_4 is substituted for $BrCCl_3$, the system is clearly S_σ. The S_π behavior is contrasted with S_σ and Br· reactivities for H abstractions from a variety of substrates and for additions to *tert*-butylethylene, isobutylene, and 1,3-butadiene. In early-transition-state systems, for H transfer, the strength of the bond being broken and the strength of the bond being made are not the major factors in determining reactivities. The behavior in late-transition-state systems is influenced by both bond strengths. The S_π radical shows intermediate behavior. These conclusions are supported by primary deuterium isotope effects for methylene chloride and chloroform: Br·, 11–13; S_π, 6; S_σ, 1.4–1.5. The Appendix addresses a number of questions raised by the preliminary study of NBS reactions by Walling et al.[31] The failure to adequately deoxygenate their reaction mixtures accounts for discrepancies in products. Their major objection to the attribution of our succinimidyl studies to S_σ and S_π is based on two points: they report rates of reaction that are stated to be too low for accommodation to our hypothesis, and they find that brominations with Br_2 in the presence of trifluoroacetic anhydride, benzoic anhydride, succinimide, or *N*-phenylsuccinimide show lower selectivity than Br·. Nonetheless, on this basis an alternate to S_σ is proposed to be a bromine atom adduct to NBS or the other carboxylic acid derivatives. This substitute proposal is not consistent with either the facts or the theoretical treatments. The arguments they base on absolute rates employ highly variable rate determinations and some assumptions in the treatment of the data that are essentially the conclusions sought.

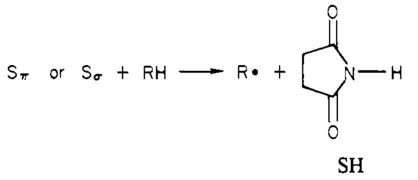
Introduction

Earlier, it was reported that the two varieties of succinimidyl radicals, π and σ, showed different selectivities for hydrogen abstraction in the one case where an unambiguous comparison was possible, neopentane and methylene chloride.[1,2] On a per hydrogen basis neopentane is 17 times as reactive as methylene chloride with S_σ, while these substrates are equally reactive with S_π. A further diagnostic is ring opening to form β-bromopropionyl isocyanate, BPI; this is a major reaction for S_σ but does not occur for S_π:



The ground state, S_π, was generated in the presence of Br_2 and the excited state, S_σ, was produced in the presence of alkenes, which served to scavenge Br_2 (eq 1–4).

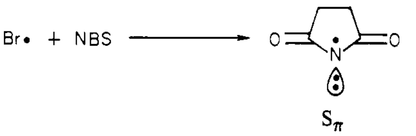
Substrates that reacted readily with Br· could not be studied unambiguously with S_π since both chain carriers might be involved simultaneously. A new method has been developed for suppressing S_σ and Br· chain carriers, by using $BrCCl_3$, in the presence of vinylidene chloride, producing S_π under conditions more broadly suitable for the study of substitution and addition reactions. That this method cleanly makes S_π for these studies is demonstrated by the absence of BPI and the rate ratio of 1.0 for the neopentane–methylene chloride competition (Table I). In the $BrCCl_3$ system it was shown that if BPI had been present, it would not have been destroyed: BPI added to the reaction mixture was recovered quantitatively.



(1)

bromine present:

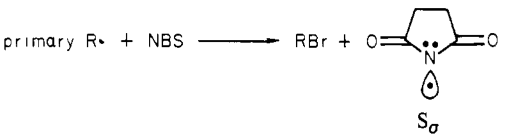
$$R\bullet + Br_2 \longrightarrow RBr + Br\bullet \qquad (2)$$



(3)

$\Delta H_3 = 0$

bromine scavenged:



(4)

$-\Delta H_4 = 21.7$ kcal/mol

The new "recipe" that gives limiting conditions in which S_π is the major chain carrier consists of the following ingredients: NBS, CH_2Cl_2 (solvent), $BrCCl_3$, and $CH_2{=}CCl_2$ (Br_2 scavenger), with $[BrCCl_3]/[CH_2Cl_2] \geq 0.32$. The reason for choosing this composition is evident from Table I, which shows the effect on BPI yields resulting from increasing amounts of $BrCCl_3$, an effect not seen when CCl_4 is used instead.

This system operates by trapping the R· radicals with $BrCCl_3$, leaving $\cdot CCl_3$ as the radical for regenerating S_π:[4]

$$S_\pi + RH \rightarrow SH + R\cdot$$

$$R\cdot + BrCCl_3 \rightarrow RBr + \cdot CCl_3$$

$$\cdot CCl_3 + NBS \rightarrow BrCCl_3 + S_\pi$$

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[1] Skell, P. S.; Day, J. C. *Acc. Chem. Res.* **1978**, *11*, 381–387.
[2] Skell, P. S.; Day, J. C. *J. Am. Chem. Soc.* **1978**, *100*, 1951.
[3] Tlumak, R. L.; Day, J. C.; Slanga, J. P.; Skell, P. S. *J. Am. Chem. Soc.* **1982**, *104*, 7257.

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Table I. Effect of Bromotrichloromethane on S_π and S_σ Production (15 °C, Photoinitiation)

	reactants			NBS	products		
expt	$[BrCCl_3]$, M	[NBS], M	$BrCCl_3/CH_2Cl_2$	conversion, %	$[BrCHCl_2]$, M	[BPI], M	$BrCHCl_2/BPI$
A	0.00	0.22	0.00	100	0.033	1.38	0.024
B	0.27	0.21	0.018	66.7	0.051	0.89	0.057
C	0.53	0.20	0.036	61.4	0.076	0.79	0.096
D	1.00	0.19	0.072	44.3	0.084	0.54	0.16
E	1.69	0.15	0.13	34.0	0.14	0.34	0.41
F	2.34	0.13	0.20	28.4	0.17	0.21	0.81
G	2.90	0.11	0.26	22.0	0.19	0.13	1.46
H	3.38	0.09	0.32	20.6	0.20	<0.09	>2.22
	$[CCl_4]$, M		CCl_4/CH_2Cl_2				
I	1.93	0.10	0.17	70.4	0.023	1.44	0.016
J	3.85	0.05	0.44	85.8	0.020	1.73	0.012

Table II. Relative Rate Constants[a] for S_σ and S_π Mediated Brominations of Neopentane and Methylene Chloride (15 °C, Photoinitiation)

	reagent system	$(k_{\text{neo-C}_5\text{H}_{12}}/k_{\text{CH}_2\text{Cl}_2})_\text{H}{}^c$	% BPI^d
S_σ	NBS, CH_2CCl_2	17	90
S_π	NBS, Br_2	1.0	0
S_π	NBS, CH_2CCl_2, $BrCCl_3$	1.1	0

[a] On a per hydrogen basis. [b] CH_2Cl_2 solvent (78.1 mmol), NBS (1.69 mmol), 1,1-dichloroethylene (0.5 mmol): $BrCCl_3$ (25.4 mmol), or Br_2 (0.13 mmol). [c] neo-C_5H_{12} (3.6 mmol). [d] Absolute yields based on NBS.

Table III. Relative Rate Constants[a] for S_σ and S_π Mediated Bromination of Neopentane, *tert*-Butyl Chloride, and 2,2-Dichloropropane (15 °C, Photoinitiation)

	reagent system[b]	$(k_{\text{neo-C}_5\text{H}_{12}}/k_{\text{t-BuCl}})_\text{H}{}^c$ (% BPI)[d]	$(k_{\text{neo-C}_5\text{H}_{12}}/k_{\text{CCl}_2(\text{CH}_3)_2})_\text{H}{}^e$ (% BPI)[d]
S_σ	NBS, CH_2CCl_2	2.3 (87)	7.4 (88)
S_π	NBS, CH_2CCl_2, $BrCCl_3$	4.1 (0)	3.4 (0)
S_π	NBS, Br_2	4.2 (0)	3.1 (0)

[a] On a per hydrogen basis. [b] CH_2Cl_2 solvent (78.1 mmol), NBS (1.69 mmol), 1,1-dichloroethylene (0.5 mmol): $BrCCl_3$ (25.4 mmol) or Br_2 (0.13 mmol). [c] neo-C_5H_{12} (3.9 mmol), *tert*-butyl chloride (9.1 mmol). [d] Absolute yields based on NBS. [e] neo-C_5H_{12} (3.9 mmol), 2,2-dichloropropane (19.7 mmol).

The $\cdot CCl_3$ does not participate in H abstractions: no $HCCl_3$ is produced, and when $DCCl_3$ is added to a reaction mixture it is recovered quantitatively, undiluted by $HCCl_3$. Benzene, a good trap for S_σ, added to this system is an inert diluent since no *N*-phenylsuccinimide is produced.[4]

S_π Selectivities

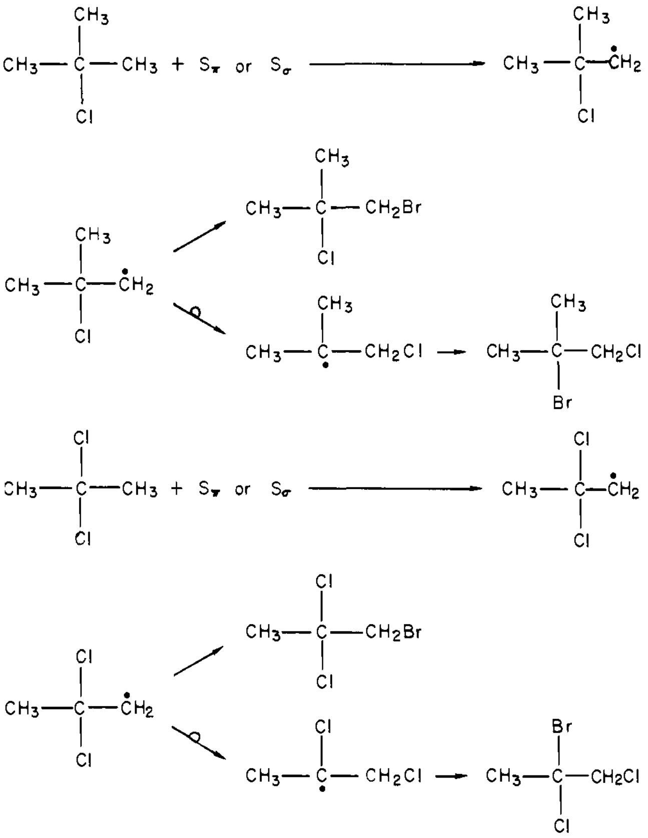
Table II compares the selectivities in the neopentane–methylene chloride competitions for S_σ and for the two methods employed for generating S_π chains. The two methods show the same selectivities and no formation of BPI; the S_σ method shows a different substitution selectivity and a large yield of BPI.

Two additional substrates that do not react readily with Br· were examined to extend the comparisons of NBS–Br_2 and NBS–$BrCCl_3$ methods: *tert*-butyl chloride and 2,2-dichloropropane (Table III). The two methods for generating the S_π carrier show nearly identical rate ratios, which differ from the S_σ rate ratios. The difference in the BPI yields confirm the assignments to S_π or to S_σ. The extent of rearrangements of Cl from C-2 to C-1 with these substrates indicates[2] that Br_2 is approximately 10^2 times faster than $BrCCl_3$ in trapping primary alkyl radicals.[5] Also, 0.2 M NBS is much slower in trapping these radicals than 2.8 M $BrCCl_3$.

A comparison of S_π and S_σ selectivities for primary and secondary C–H bonds was made with butane (Table IV). The effective exclusion of Br· and $\cdot CCl_3$ chain carriers is evident.

The intramolecular competitions with 1-bromobutane were

Scheme I



reagent system	substrate	% unrearranged product	% rearranged product
NBS, Br_2 (0.26 M)	*tert*-butyl chloride	55 55	45
NBS, Br_2 (0.03 M)	*tert*-butyl chloride	11	89
NBS, Br_2 (0.16 M)	2,2-dichloropropane	90	10
NBS, Br_2 (0.08 M)	2,2-dichloropropane	75	25
NBS, CH_2CCl_2, $BrCCl_3$ (2.82 M)	*tert*-butyl chloride	14	86
NBS, CH_2CCl_2	*tert*-butyl chloride	<2	98

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(4) Tlumak, R. L.; Skell, P. S. *J. Am. Chem. Soc.* **1982**, *104*, 7267.

(5) These two sets of experiments have another point of interest since the unimolecular rearrangement of the chloro substituent to the radical site competes with the trapping of the primary alkyl radicals that are initially produced. While the preliminary trapping results do not allow for a detailed kinetic analysis, they do indicate that trapping of the unrearranged radical is equally efficient by 0.03 M Br_2 and 2.8 M $BrCCl_3$, making their rate ratio for trapping primary alkyl radicals $k_{Br_2}/k_{BrCCl_3} \sim 10^2$ (see Scheme I). For an earlier report on the unexpected low rates of reaction of radicals with NBS see: Skell, P. S.; Tuleen, D. L.; Readio, P. D. *J. Am. Chem. Soc.* **1963**, *85*, 2850.

Table IV. Substitution Yields for S_σ and S_π toward Butane (15 °C, Photoinitiation)

	reactants	butane, %		BPI, %[c]
		C-1	C-2	
S_σ	NBS, CH_2CCl_2[a]	30	70	82
S_π	NBS, CH_2CCl_2, $BrCCl_3$[b]	11	89	0
$\cdot CCl_3$	(27 °C)[27]	0.8	99.2	
Br·	(27 °C)[21]	0.2	99.8	

[a] CH_2Cl_2 solvent (78.1 mmol), NBS (1.69 mmol), 1,1-dichloroethylene (0.5 mmol), *n*-butane (3.91 mmol). [b] Identical with *a*, except $BrCCl_3$ (25.4 mmol) was added. [c] Absolute yields based on NBS.

examined with S_π and with S_σ, the latter made with the $BrCCl_3$ "recipe" (Table V). The S_σ selectivity is similar to that reported with Cl· chlorinations,[6] showing deactivation at C-2 relative to C-3. The S_π resembles Br· attack on this substrate,[6,7] showing a marked anchimeric assistance by the bromine substituent for abstraction of a C-2 hydrogen, but smaller than that observed with Br·.[7] Photoinitiation and thermal initiation with peroxides show the same product distribution for these chain reactions.

Substitution selectivities for S_π and S_σ toward isobutane are shown in Table VI. Isobutane reactions with the S_π system give unambiguous selectivities: S_π strongly prefers tertiary C–H bonds. Interpretation of experiments with isobutane in the S_σ system requires the information that the reaction of *tert*-butyl radical with NBS produces a 96:4 mixture of S_σ and S_π.[3] With this knowledge the contribution of S_π can be subtracted, to give for pure S_σ plus isobutane the products isobutyl bromide (39%) and *tert*-butyl bromide (61%).

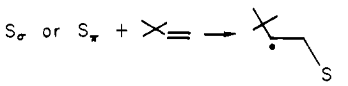
The addition chemistry of NBS to 1,3-butadiene has been reported previously:[3] formation of an allylic radical intermediate, **2** (eq 5), which was subsequently trapped by NBS to give S_π and

$$S_\sigma \text{ or } S_\pi + CH_2{=}CHCH{=}CH_2 \rightarrow \underset{\mathbf{2}}{CH_2\cdots\dot{C}H\cdots CHCH_2S} \qquad (5)$$

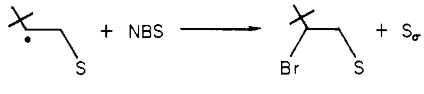
$$\mathbf{2} + NBS \rightarrow BrCH_2CH{=}CHCH_2S + S_\pi \text{ (major)} \qquad (6)$$

$$\mathbf{2} + NBS \rightarrow CH_2{=}CHCHBrCH_2S + S_\pi \text{ (minor)} \qquad (7)$$

predominantly the 1,4-adduct. Also, the addition of succinimidyl to 3,3-dimethyl-1-butene has been reported,[8,9] leading ultimately to *N*-(2-bromo-3,3-dimethyl-1-butyl)succinimide and S_σ (eq 9).



(8)



(9)

These same products are obtained in the presence of benzene, an efficient trap for S_σ. A competition reaction between 1,3-butadiene (1.30 mmol, 0.15 M) and 3,3-dimethyl-1-butene (2.3 mmol, 0.32 M) yielded the products *N*-(2-bromo-3,3-dimethyl-1-butyl)succinimide (0.060 mmol), 1,3-butadiene addition products (1.10 mmol) and $BrCHCl_2$ (0.081 mmol). These results are consistent with S_π generation via the reactions of **2** with NBS (reactions 6 and 7) and thus allows one to assign an S_π origin to these products, $k_{CH_2(CH)_2CH_2}/k_{CH_2CH\text{-}t\text{-}Bu} = 33.0$, and for the relative rate of H abstraction from CH_2Cl_2 to addition, $k_{CH_2Cl_2}/k_{CH_2CH\text{-}t\text{-}Bu} = 0.040$. For S_σ, earlier work led to relative rates 3.7[4] and 0.0020,[3] respectively.

The results of an experiment in which 3,3-dimethyl-1-butene and isobutylene compete for S_π indicate that methallyl bromide is the major product from isobutylene, accompanied by some addition product. Since no BPI was detected in the product mixture, this result is rationalized with the generation of S_π from the reaction of methallyl radical with NBS.[4] From an experiment in which 3,3-dimethyl-1-butene (1.6 mmol, 0.21 M) and isobutylene (1.0 mmol, 0.14 M) were reacted, the addition products were *N*-(2-bromo-3,3-dimethyl-1-butyl)succinimide (0.016 mmol) and *N*-(2-bromo-2-methyl-1-propyl)succinimide (0.016 mmol), from which it follows that for S_π additions, $k_{10}/k_7 = 6.9$.

Table V. Substitution Yields for S_σ and S_π toward 1-Bromobutane[a] (15 °C, Photoinitiation)

	reagent system	1-bromobutane, %				BPI, %[b]
		C-1	C-2	C-3	C-4	
S_σ[d]	NBS, CH_2CCl_2[c]	9	25	46	20	73 73
S_π[e]	NBS, CH_2CCl_2, $BrCCl_2$	3	65	27	5	0
Br·	NBS, Br_2[7]	0	89	11	0	0

[a] CH_2Cl_2 solvent (78.1 mmol), NBS (1.69 mmol), 1,1-dichloroethylene (0.5 mmol), $BrCCl_3$ (25.4 mmol), and 1-bromobutane (18.7 mmol). [b] Absolute yields based on NBS. [c] 1,1-Dichloroethylene and 3,3-dimethyl-1-butene are suitable as bromine scavengers, each system showing the same selectivities. [d] A peroxide-initiated reaction (35 °C) made dibromobutane in relative yields of 10%, 24%, 45% and 20% with a 72% yield of BPI. [e] A peroxide-initiated reaction made dibromobutanes in relative yields of 6%, 61%, 31% and 2% at 35 °C, and 2%, 67%, 27% and 9% at 77 °C; in both cases BPI was not a product.

Table VI. Substitution Yields for S_σ and S_π toward Isobutane (15 °C, Photoinitiation)

	reactants	isobutane, %		BPI, %[c]
		C-1	C-2	
S_σ (+S_π)	NBS, CH_2CCl_2[a]	38	62	71
S_π	NBS, CH_2CCl_2, $BrCCl_3$[b]	3	97	0
$\cdot CCl_3$	(27 °C)[27]	0.03	99.97	
Br	(27 °C)[21]	0.006	99.994	

[a] CH_2Cl_2 solvent (78.1 mmol), NBS (1.69 mmol), 1,1-dichloroethylene (0.5 mmol), isobutane (3.95 mmol). [b] Identical with *a*, except $BrCCl_3$ (25.4 mmol) was added. [c] Absolute yield based on NBS.

(10)

3

(11)

To determine the analogous rate ratio for this olefin pair adding S_σ, the isobutylene–*tert*-butylethylene competition was studied under the same conditions, except for omission of benzene, which makes this into a system operating mainly with S_σ. The results are given in Table VII. The ratio $BrCHCl_2$ to BPI is 0.040; if it had been a pure S_σ system, a value of 0.022 should have been observed.[3] This corresponds to a small contribution from S_π (made from reactions of NBS with (a) methallyl radical, 0.028 mmol, and (b) 4.3% of the tertiary radical[4] **3**, 0.014 mmol). Thus, the addition products, which total 0.53 mmol, can be attributed almost exclusively to S_σ, and it becomes possible to evaluate for additions of S_σ, $k_{CH_2C(CH_3)_2}/k_{CH_2CH\text{-}t\text{-}Bu} = 1.8$.

Selectivities of S_π and S_σ. Early and Late Transition States

The development of the new system in which the chemical properties of S_π may be examined allows for more extensive comparisons with the behavior of S_σ than was possible earlier. The relative rates for all the reactions of S_π relative to addition to 3,3-dimethyl-1-butene are summarized in Table VIII and compared with the S_σ rates.

The selectivity in additions of S_π to alkenes is a familiar one: 1,3-butadiene is faster than isobutylene, which is faster than

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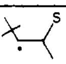
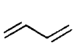
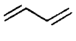
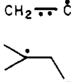
(6) Thaler, W. A. *J. Am. Chem. Soc.* **1963**, *85*, 2607.
(7) Skell, P. S.; Shea, K. J. *J. Am. Chem. Soc.* **1963**, *85*, 2607.
(8) Slanga, J. P.; Day, J. C.; Skell, P. S. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 7, 515.
(9) Skell, P. S.; Day, J. C.; Katsaros, M. G.; Kocher, W. D.; Scott, A. E. *J. Am. Chem. Soc.* **1978**, *100*, 1950.

Table VII. Competition between 3,3-Dimethyl-1-butene and Isobutylene for S_σ (15 °C, Photoinitiation)

reactants, mmol (M)	products, mmol[a]
3,3-dimethyl-1-butene, 1.55 (0.29)	*N*-(2-bromo-3,3-dimethyl-1-butyl)succinimide, 0.21
isobutylene, 1.20 (0.23)	*N*-(2-bromo-2-methyl-1-propyl(succinimide, 0.32
NBS, 1.69	methallyl bromide, 0.028
CH_2Cl_2, 78 (14.7)	$BrCHCl_2$, 0.042
	BPI, 1.05
	succinimide, 0.070

[a] Reaction carried to 100% conversion of NBS.

Table VIII. Relative Rate Constants[a] for Several Reactions of S_π and S_σ

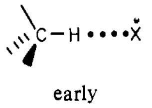
substrate	product radical	rel rate constants	
		S_π	S_σ
		(1.0)	(1.0)
	$CH_2 \cdots \dot{C}H \cdots CHCH_2S$	33	3.7
		6.9	1.9
CH_2Cl_2	$CHCl_2\cdot$ + SH	0.036	0.0015
neo-C_5H_{12}	neo-$C_5H_{11}\cdot$ + SH	0.21	0.15
butane	*sec*-butyl· + SH	0.85	0.18
isobutane	*tert*-butyl· + S'I	81	0.32
1-bromobutane	1-bromo-2-butyl· + SH	0.46	0.047

[a] Relative to addition to 3,3-dimethyl-1-butene, on a per molecule basis.

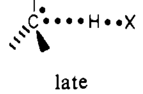
tert-butylethylene. The selectivity of S_σ is unexpected in that it shows slight differentiation between the alkenes. This supports our suggestion that S_σ reactions are best interpreted with early transition states.

The reactivities of S_π and S_σ for H abstractions are summarized in Table IX along with data for a number of other radicals, arranged in a sequence that gives the alkanic reactivities a monotonic order, with the most selective X· at the bottom of the list.

The upper X· of this table show an insensitivity to both the H–X bond being made and the C–H bond being broken. The lower X· show sensitivity to the strengths of both bonds. This behavior is best explained with two transition states for H abstraction, an early one for the upper X· and a well-developed transition state for the lower X·. The S_σ reacts with an early transition state, the S_π with a well-developed one.



early
transition state



late
transition state

The withdrawal of electron density from the C–H bonds by the chloro substituent can explain the low reactivity of CH_2Cl_2 in early-transition-state reactions. In the later-transition-state reactions, this effect is less pronounced, and stabilities of the products exert a dominant influence.

The rates of reactions at the four carbons of 1-bromobutane (Table X) show an analogous response to variations of X·. The anchimeric assistance effect at C-2[6,7,26] is most evident for Br· and is still noticeable for S_π. The greater exothermicity and earlier transition states for Cl·, S_σ, and *t*-BuO· reactions preclude assistance from the bromo substituent and thus give the expected pattern of reduced reactivity at C-2.

Primary Deuterium Isotope Effects for S_σ, S_π, and Br Hydrogen Abstractions

The chloroform isotope effects were determined from the relative rates of bromination for $CHCl_3$–CH_2Cl_2 and $CDCl_3$–CH_2Cl_2; in both systems the yields of bromotrichloromethane and bromodichloromethane were determined by gas chromatography.

The methylene chloride isotope effects were determined in two ways: (1) directly on CH_2Cl_2–CD_2Cl_2, the total yield of bromodichloromethanes being determined by gas chromatography, and the yield of $BrCHCl_2$ by 360-mHz proton magnetic resonance; (2) by competitions between neopentane–CH_2Cl_2 and neopentane–CD_2Cl_2, with gas chromatography used to determine yields.

All analytical methods were verified with known product mixtures. The direct comparison of CH_2Cl_2–CD_2Cl_2 was checked for exchange between dichloromethyl radical and unreacted substrate by determining with mass spectrometry–gas chromatography the amount of $CHDCl_2$; this substance, if present after bromination, was in amounts below our detection limit of 1%.

Bromine atom chain carrier was studied by using photoinitiation of Br_2 in the presence of an excess of anhydrous K_2CO_3, which serves as a totally satisfactory HBr scavenger,[28] thus eliminating the difficulties that are attributable to reversal (reaction of radicals with HBr). This method is complementary to the method employed earlier, scavenging with NBS.[29]

S_σ chain carrier was studied with photoinitiation of solutions saturated with NBS, employing vinylidene chloride (VC) as the Br_2 scavenger.

S_π chain carrier was studied with photoinitiation, with NBS–Br_2 for chloroform and with NBS in the presence of VC and $BrCCl_3$ for methylene chloride.

These experiments are summarized in Tables XI and XII. At high $[Br_2]/[NBS]$ ratios chloroform is brominated by a Br· chain carrier, exactly as was reported earlier for bromination of butane.[1] In the presence of a bromine scavenger the hydrogen abstractor (S_σ) resembles Cl·. With $[Br_2]/[NBS]$ less than 0.9 the k_H/k_D ratio decreases until it reaches a new plateau value of 6.3, attributed to S_π. An alternate method for isolating S_π behavior, which will be reported elsewhere, employing benzene to scavenge S_σ, gives values of 6.4 and 6.3.

With the methylene chloride system a much higher ratio of $[Br_2]/[NBS]$ is required to reach the Br· value. The S_σ value is again similar to that shown by Cl·. The $BrCCl_3$ method for isolating S_π behavior gives intermediate values of 5.8 and 5.9.

The isotope effects for methylene chloride and chloroform show different values for the three chain carriers. These values are consistent with the rationalization that Br· abstracts H in a well-developed transition state[30] and with our proposal that S_σ abstracts with an early transition state and S_π abstracts in an intermediate fashion.

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(10) Darwent, B. de B. "Bond Dissociation Energies in Simple Molecules"; National Bureau of Standards: Washington, DC, 1970; NSRDS-NBS 31.

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

(12) Kerr, J. A. *Chem. Rev.* **1966**, *66*, 465.

(13) Reed, K. J.; Brauman, J. L. *J. Am. Chem. Soc.* **1975**, *97*, 1625.

(14) Mendenhall, G. D.; Golden, D. M.; Benson, S. W. *J. Phys. Chem.* **1973**, *77*, 2707.

(15) Gaydon, A. G. "Dissociation Energies and Spectra of Diatomic Molecules", 3rd ed.; Chapman and Hall: London, 1968.

(16) Deno, N. C.; Fishbein, R.; Wyckoff, J. C. *J. Am. Chem. Soc.* **1971**, *93*, 2065.

(17) Russell, G. A. *J. Am. Chem. Soc.* **1958**, *80*, 4997.

(18) Greiner, N. R. *J. Chem. Phys.* **1970**, *53*, 1070, 1285.

(19) Walling, C.; Jacknow, B. B. *J. Am. Chem. Soc.* **1960**, *82*, 6108.

(20) McGrath, B. P.; Tedder, J. M. *Bull. Soc. Chim. Belg.* **1962**, *71*, 772.

(21) Fettis, G. C.; Knox, J. H. *Prog. React. Kinet.* **1964**, *2*, 3.

(22) Golden, D. M.; Benson, S. W. *Chem. Rev.* **1969**, *69*, 125.

(23) Furuyama, S.; Golden, D. M.; Benson, S. W. *J. Am. Chem. Soc.* **1969**, *91*, 7564.

(24) Fettis, G. C.; Knox, J. H. "Progress in Reaction Kinetics"; Porter, G., Ed.; Macmillan: New York, 1967; Vol. 2.

(25) Ody, K.; Nechvatal, A.; Tedder, J. M. *J. Chem. Soc., Perkin Trans. 2* **1976**, 521.

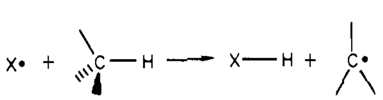
(26) Skell, P. S.; Shea, K. J. "Free Radicals"; Kochi, J., Ed.; Wiley: New York, 1973; pp 809–850.

(27) Wampler, F. B.; Kuntz, R. R. *Int. J. Chem. Kinet.* **1971**, *3*, 483.

(28) Tanner, D. D.; Arhart, R. J.; Blackburn, E. V.; Das, N. C.; Wada, N. *J. Am. Chem. Soc.* **1974**, *96*, 829.

(29) Shea, K. J.; Lewis, D. C.; Skell, P. S. *Ibid.* **1973**, *95*, 7768.

Table IX. Partial Relative Rate Constants[a] for



BDE, kcal/mol (X–H)	X· (temp, °C)	alkanic C–H bonds				
		1°	2°	3°	CH_2Cl_2	$CHCl_3$
	$Me_2N^{+}\cdot$ (15)[16]	1.0	2.9	3.1		
103.2[10]	Cl· (25)[17]	1.0	3.6	4.2	0.02[24]	
114–118[11]	S_σ (15)	1.0	3.5	14.1	0.06	0.0014
119[12]	·OH (25)[18]	1.0	7	45		
105.1[13]	*t*-BuO· (20)[19]	1.0	9.2	53.6		
~100[11]	S_π (15)	1.0	12.1	291	1.0	2.14
95.8[14]	$\cdot CCl_3$ (20)[20]	1.0	200	7000		
87.4	Br· (27)[21]	1.0	640	25000	10.0	8.5
	BDE ± 1, kcal/mol	98–103[22]	95[22]	92[22]	99[23]	96

[a] On a per hydrogen basis.

Table X. Halogenation of 1-Bromobutane: Relative Reactivities[a] at Each Carbon

	reagent (°C)	1-bromobutane				
		C-1	C-2	C-3	C-4	ref
	Cl_2 (60)	0.09	0.43	1.0	0.46	6
S_σ	NBS, CH_2CCl_2 (15)	0.20	0.54	1.0	0.43	
	t-BuOCl (25)	0.38	0.58	1.0	0.25	25
	t-BuOBr (25)	0.59	0.73	1.0	0.15	25
S_π	NBS, CH_2CCl_2, $BrCCl_3$ (15)	0.11	2.4	1.0	0.19	
	Br_2 (15)	0	8.3	1.0	0	7

[a] *Not* based on the number of hydrogens at each carbon.

Experimental Section

General Procedures. ^1H NMR spectra were recorded on a Varian EM-360 spectrometer with chemical shifts reported on the δ scale relative to Me_4Si. Infrared analyses were carried out on a Perkin-Elmer 580 or 727 spectrometer. Gas chromatography analyses were carried out on a Varian 1400 FID using a 60/80 Carbopack B 1% SP-1000 6 ft × 2 mm or a 100/120 Chromosorb Q 10% Silar 10 6 ft × 2 mm column.

Materials. *N*-Bromosuccinimide was obtained from Aldrich Chemical Co. Methylene chloride was purified by successive extraction with concentrated H_2SO_4, distilled water, and 5% aqueous sodium bicarbonate solution, dried with anhydrous calcium chloride and distilled from phosphorous pentoxide. 3,3-Dimethyl-1-butene and 1,1-dichloroethylene were obtained from Aldrich, the former used as received, the latter vacuum distilled prior to use. Bromotrichloromethane (Aldrich) 2,2-dichloropropane (Columbia Organic Chemical Co.), *tert*-butyl chloride (Eastman), and 1-bromobutane (Aldrich) were each washed with concentrated H_2SO_4 and distilled prior to use. Benzene employed in this work was distilled from Na-K alloy before use. Neopentane (Phillips, 99%) was used without further purification. *n*-Butane and isobutane (Matheson, 99%) were used as received. 1,3-Butadiene and isobutylene were obtained from Matheson (99%), the former dried over anhydrous $CaSO_4$ prior to use, the latter used as received.

Photolysis Experiments. All reactions were carried out in 30-mL capacity Pyrex pressure tubes sealed with Teflon needle valves. Reactant mixtures were degassed three times by a freeze–thaw technique with freezing and evacuating at −196 °C and thawing at ambient temperature. The sealed pressure tube, in a Pyrex water-circulating bath maintained at ~14–15 °C, was irradiated with a 400-W medium-pressure mercury arc.

Typically, the NBS, CH_2Cl_2, $BrCCl_3$ or C_6H_6, and substrate were transferred to the pressure tube and degassed. Gaseous reactants and volatile alkenes were separately degassed and condensed into the reaction tube, which was then sealed and irradiated. Irradiation times of 0.5–1.5 h were employed. Product yields were obtained from direct ^1H NMR integrations employing an internal standard (hexamethyldisiloxane). Alternatively, yields of brominated substrates were determined by gas chromatography after addition of internal standard (chlorobenzene) and workup (aqueous $NaHSO_3$, aqueous $NaHCO_3$, and Na_2SO_4). A third method involved the separation of the volatile and nonvolatile materials by vacuum trap-to-trap distillation (1 mmHg) into a −196 °C trap. The nonvolatile materials were analyzed by ^1H NMR and the volatile materials by GC without workup. Products were identified by commparison of GC retention times and/or spectra of authentic samples.

Authentic samples of most of the brominated substrates obtained in this work are commercially available. The preparation and spectral properties of β-bromopropionyl isocyanate, *N*-(2-bromo-3,3-dimethyl-1-butyl)succinimide, *N*-phenylsuccinimide, 1-bromo-4-succinimidyl-2-butene, and 3-bromo-4-succinimidyl-1-butene have been described previously.[3,6]

N-(2-bromo-2-methyl-1-propyl)succinimide was isolated from the reaction of NBS (0.50 g, 2.81 mmol) with isobutylene (8.00 mmol) in CH_2Cl_2 solvent after removal of the volatile materials in vacuo and recrystallization of the solid residue from hexane (0.41 g, 62% yield); mp 123–124 °C; ^1H NMR ($CDCl_3$) δ 1.7 (s, 6 H), 2.75 (s, 4 H), 3.9 (s, 2 H).

Compositions of individual reaction and product mixtures are given in Tables I–IX. Relative rate constant ratios for Tables I and II were calculated by using the yields of brominated substrates and the equation

$$[k_{neo\text{-}C_5H_{12}}/k_{substrate}]_H = ([neo\text{-}C_5H_{11}Br][substrate]/[neo\text{-}C_5H_{12}][brominated\ substrate])/N$$

where $N = 1.33$, 2.0, and 6.0 for *tert*-butyl chloride, 2,2-dichloropropane, and CH_2Cl_2, respectively. Bromination of *tert*-butyl chloride leads to two products that are clearly distinguishable by ^1H NMR, 1-bromo-2-chloro-2-methylpropane (δ 1.7 (s, 6 H), 3.7 (s, 2 H)) and the rearranged product 2-bromo-1-chloro-2-methylpropane (δ 1.8 (s, 6 H), 3.85 (s, 2 H)). Bromination of 2,2-dichloropropane also leads to two products that are clearly distinguishable by ^1H NMR, 1-bromo-2,2-dichloropropane (δ 2.25 (s, 3 H), 3.95 (s, 2 H)) and the rearranged product 2-bromo-1,2-dichloropropane (δ 2.35 (s, 3 H), 4.1 (s, 2 H)). These compounds were also identified by their elimination of potassium halide in alcoholic KOH at 50 °C and by spectroscopic comparison of the isolated olefins to authentic samples.

Acknowledgment. This work was carried out with financial support from the National Science Foundation.

Appendix. A Response to Walling, El-Taliawi, and Zhao[31]

Background. This unusual treatment of the subject is occasioned by the preceding paper,[31] which the authors (WEZ) characterize as preliminary, the intent of which is stated to be prevention of entrenchment of the S_π–S_σ hypothesis we proposed.

We would like to point out that there are both observational differences and interpretative differences between our two laboratories. There has been a free exchange of manuscripts, with the result that some of the early areas of experimental disagreement have been removed from the WEZ paper. Nonetheless, a number remain despite persistent efforts to resolve them.

Oxygen Removal. One of these disagreements has to do with the amount of ring-opened product, BPI, obtained in NBS–$CHCl_3$–vinylidene chloride (VC) systems: in Utah BPI is reported as a significant product, whereas in State College none was

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(30) (a) Lewis, E. S.; Kozuka, S. *J. Am. Chem. Soc.* **1973**, *95*, 282. (b) Lewis, E. S. "Isotopes in Organic Chemistry"; Buncel, E., Lee, C. C., Eds.; Elsevier Scientific: New York, 1976; Vol. 2, pp 127–152. (c) Lewis, E. S. *Top. Cur. Chem.* **1978**, *74*, 32.

(31) Walling, C.; El-Taliawi, G. M.; Zhao, C. *J. Am. Chem. Soc.*, preceding article in this issue.

Table XI. Relative Rates of Reaction for CH_2Cl_2/CD_2Cl_2 (15 °C, photoinitiation)

	method	$k(+/CH_2Cl_2)_{\text{per H}}$	$k(+/CD_2Cl_2)_{\text{per H}}$	$k(CH_2Cl_2/CD_2Cl_2)$	k_H/k_D
Br·	Br_2–K_2CO_3	0.064	0.729		11.40
	Br_2–K_2CO_3			11.70	11.70
	$[Br_2]/[NBS] \geqslant 5.2$			11.48	11.48
S_π	NBS–$BrCCl_3$–VC	0.95	5.64		5.93
		0.99	5.72		5.77
S_o	NBS–VC			1.47	1.47
				1.51	1.51

Table XII. Relative Rates of Reaction for $CHCl_3/CDCl_3$ (15 °C, photoinitiation)

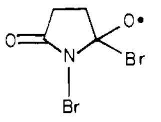
	method	$k(CH_2Cl_2/CHCl_3)_{\text{per mol}}$	$k(CH_2Cl_2/CDCl_3)_{\text{per mol}}$	k_H/k_D
Br·	Br_2–K_2CO_3	2.27	29.81	13.10
		2.41	30.70	12.70
	$[Br_2]/[NBS] \geqslant 0.9$	2.31[a]	29.82	12.90
		2.34[b]	30.40	13.00
S_π	$[Br_2]/[NBS] \leqslant 0.009$	0.94	5.84	6.21
		0.87	5.50	6.32
S_σ	NBS–VC	7.24	9.92	1.37
		7.06	10.30	1.46

[a] $[Br_2]/[NBS] = 5.8$. [b] $[Br_2]/[NBS] = 0.9$.

found.[1-4,8,9] Ultimately we found the difference is attributable to the methods employed for the removal of oxygen. If oxygen is removed by vacuum degassing, BPI is not a product in these $CHCl_3$–VC systems. All of our experiments were carried out in vacuum-tight systems after multiple high-vacuum degassing of the reaction mixtures. The Walling et al. procedure involves flushing with argon in NMR tubes, followed by insertion of a plastic cap (the WEZ kinetic experiments were carried out in sealed tubes after argon flushing). We conclude the flushing procedure is not adequate for the removal of oxygen.

BPI Reaction Channel Requires Vinylidine Chloride. In a further examination of the sources of the disagreement we confirmed our claim that the presence of vinylidene chloride is strictly required for preclusion of BPI, just as we stated earlier[4] and in the current paper. An experiment was carried out in an NMR tube, employing our method for excluding oxygen: 0.185 mmol NBS, 6.20 mmol $CHCl_3$, 0.029 mmol CH_2CCl_2, and 0.017 M $(C_6H_5CO_2)_2$, maintained at 50 °C in the dark, monitored frequently by NMR. Up to 96 h there is no BPI produced, but a steady decrease in the vinylidene chloride concentration is observed, the concentration at the end of that time period falling to a value below the detection limit. After 96 h BPI *is* produced. The experiment is wholly consistent with our earlier rationalization[3,4] of a similar occurrence.

Carbonyl Additions: The WEZ Proposal. The *agreement* of interpretation between the principals is that there are present in these NBS systems *three potential hydrogen-abstracting chain carriers*. We identify these as S_σ, S_π, and Br, and they identify them as (1) succinimidyl, (2) a complex of Br with succinimide or NBS, for which two structures (I and II) are proposed, and



I

$C_4H_4O_2N$—Br—Br

II

(3) Br. The inspiration for these Br complexes is their reported observations (WEZ Table I) that the relative rates of photobrominations of neopentane–methylene chloride mixtures are substantially altered if certain substances are included in the reaction mixtures: trifluoroacetic anhydride, benzoic anhydride, succinimide, or *N*-phenylsuccinimide. We fail to see how these complexes could explain additions of succinimidyl to unsaturated compounds under our S_π conditions (this paper and ref 4). But our most important objection is contained in the main body of our paper: our selectivities, which Walling et al. attribute to a bromine atom complex, are also found for systems in which Br and Br_2 are scavenged by vinylidene chloride.

Primary Deuterium Isotope Effects. There was earlier disagreement on the subject of deuterium isotope effects, and there continues to be substantial disagreement here. Currently WEZ report primary deuterium isotope relative rate values of 9.6–10.6 for NBS brominations of CH_2Cl_2–CD_2Cl_2 mixtures, in *both* the presence or absence of Br_2 (VC as scavenger), results strikingly different from ours. Both of their values approximate our values (11.5–13.0) for pure Br· H abstractions (absence of NBS, or in the presence of NBS if $[Br_2]$ is large enough to overwhelm the S_π chain). We find that if alkene is present k_H/k_D is 1.5; this is our S_σ value, and it is consistent with our suggestion of an early-transition-state H abstraction. If the $[Br_2]$ concentration is low enough to make the S_π the major H abstractor, then k_H/k_D is 6.0. We obtain this same value when Br_2 is scavenged by VC if sufficient $BrCCl_3$ is present to make S_π the main chain carrier.

We can understand the WEZ value with NBS–Br_2 since their ratio of these reactants is 3.14, approximately the minimum ratio (5.2) we have determined for Br_2 to completely overwhelm the S_π chain. The WEZ value in the presence of vinylidene chloride eludes our understanding at present; we will address this question in the near future.

Basis for Our High Rate Constant Assignments. We had chosen to avoid the well-known hazards attending efforts to extract absolute rate constants for elementary steps from overall rates in chain reactions. We used the overall rates solely to demonstrate that we were concerned with chain reactions (quantum yields proved to be considerably larger than unity).[3]

For the rest we used the more reliable method of determining rate constant ratios for competitive processes. We based our 1978 approximation of high absolute rate constants on the observations that under S_σ conditions, relative rates of H abstractions, additions to alkenes, and additions to arenes closely resembled those known for Cl· and OH·.[1] These latter two are recognized to react with near encounter-controlled rate constants, and for this reason we suggested similarly large rate constants might apply for S_σ chemistry. Walling offers no rationalization for this extraordinary similarity of relative rate constants.

Absolute Rate Constants from Overall Rates. Walling and co-workers oppose this proposal on the basis that (1) the absolute rate constants they calculate are much smaller than we suggest, and (2) the "S_σ conditions" give lower rates than the "S_π conditions", the opposite of what would be expected for high- and low-energy intermediates, respectively. They claim the rate constants in question are 10^3–10^4 L mol^{-1} s^{-1} and that these are inconsistent with our suggestions. Their rate constants are obtained from a very limited examination of the problem.

First, in our hands the systems containing olefin (S_σ) always react much faster than those containing bromine (S_π or Br) or those containing bromotrichloromethane and vinylidene chloride (S_π). Second, determinations of absolute rate constants for chain steps from overall rates are notoriously misleading since they depend critically on the effects of inhibitors (either from reagents or from those generated in the reactions, or from O_2, etc.) and because of the uncertainties regarding initiator efficiencies. For example, we are surprised that WEZ find only a small decrease in their rates if they use Aldrich inhibited vinylidene chloride in place of inhibitor-free material. We find that the inhibited Aldrich vinylidene chloride has a powerful effect in slowing down NBS reactions that are high-vacuum degassed. This failure to obtain strong inhibition from the hydroquinone monomethyl ether (the Aldrich inhibitor) may be an indication of the presence of other inhibitors in the WEZ system. Further, we find that after carrying out a reaction, under our best inhibitor-free conditions, the nonvolatile residue contains inhibitors, which when introduced into fresh reactants causes a diminution of the rate. Thus, we believe the WEZ systems contained oxygen and inhibitors, some from the reagents and some produced during the reactions, making their overall rates a suspect source for the calculations of the absolute rate constants of the elementary steps.

Absolute Rate Constants by Analogy with the Yip, Chow and Beddard[32] Glutarimidyls. Walling supports his conclusion that imidyl radicals do not react with rate constants of 10^7–10^9 L mol^{-1} s^{-1}, as he states we suggested for S_σ, by citing the kinetic flash photolysis report of Yip, Chow, and Beddard, particularly the value $k_2 = 3500$ for *glutarimidyl* reacting with cyclohexane.

First, we suggested[3] for *σ-succinimidyl*, S_σ, the following absolute rate constants: 2×10^7 s^{-1} for ring-opening of S_σ, 1×10^7 M^{-1} s^{-1} for S_σ additions to *tert*-butylethylene, and 1×10^6 M^{-1} s^{-1} for H abstraction from neopentane by S_σ. (These values are based on reliable relative rates[3] and the assumption that the rate constant for alkyl radicals reacting with Br_2 is near the encounter-controlled limit: we use a value of 1×10^{10} M^{-1} s^{-1} for trapping by Br_2 to calculate our absolute rate assignments.)

Second, we read the YCB report for glutarimidyl differently than WEZ. YCB recognize two radicals named "precursor" and "transient", precursor decaying to transient at a rate $>2 \times 10^5$ s^{-1}. Their concluding statement is "*The precursor is possibly another electronic state of the observed imidyl radical* or, alternatively, an excited state of the *N*-bromoglutarimide". (The so-called observed radical is their "transient". Of course, both "precursor" and "transient" are spectroscopically observed species.) They report the precursor adds to *tert*-butylethylene with a rate constant $>2 \times 10^8$ L mol^{-1} s^{-1}. We believe this can be an argument in favor of the former alternative they offer: the precursor *is* excited state glutarimidyl. We cannot envision a reaction of excited state *N*-bromoglutarimide that would result in additions of the glutarimidyl portion to the alkene. If an excited state of NBG did add to the alkene, it seems reasonable that the Br portion would add, leaving a G· fragment, the opposite of what is observed: the presence of olefin decreases the concentration of G·. We find that the Yip et al. data for glutarimidyl are remarkably consistent with the values of rate constants we assigned to the σ-succinimidyl radical. Work in progress on glutarimidyl radical chemistry indicates (a) two radicals are involved and (b) the energy separation seems to be smaller than for the succinimidyls.

Absolute Rate Constants for π-Imidyls. Unfortunately, none of our methods has been suitable for estimating absolute rates for either S_π or G_π, and consequently we have made no suggestions as to what these values might be. If our understanding of the YCB work is proven correct, the rates they assign to their transient are those for G_π·: for addition to *tert*-butylethylene, $k = 9 \times 10^6$ M^{-1} s^{-1}, and for H-abstraction from cyclohexane, $k = 3.5 \times 10^3$ M^{-1} s^{-1}.

Absolute Rates Constants by Analogy with Studies of Amidyl Radicals. Walling also cites a rate constant of 6.4×10^3 M^{-1} s^{-1} for H abstraction from cyclohexane by a π-amidyl radical, Et-$\dot{N}$–COET.[33] The relevance of this argument is doubtful. But nonetheless the subject is of considerable interest since the possibility of π and σ radicals in amidyl systems has not been adequately recognized. The extensive work of Lessard and coworkers[34] is recognizably concerned with a highly selective type of amidyl radical, with little doubt the π state.[35] When comparisons are made between the Lessard amidyl chemistry and the amidyl radical chemistries described by Johnson and Greene[36] and Joseph et al.,[37] it becomes apparent that amidyl radicals show a variety of behaviors, depending on what scavengers are present, in the latter two studies, including H abstractions from unactivated methyl groups. Clearly the amidyl system also shows π and σ behaviors.

ESR Report on Ground-State π-Succinimidyl. There is now an ESR report[38] describing a succinimidyl radical, generated by X-irradiation of succinimide, which is clearly the π state. It is stable and, therefore, in the ground state. The authors were not able to find any evidence of ring opening to $\cdot CH_2CH_2CONCO$ (PI).

Theoretical Treatments. While it is agreed that current state-of-the-art calculations may yield accurate energy relations and that less sophisticated calculations are not as trustworthy, nonetheless, the latter have given ample evidence of their utility. Prior to our work Koenig and Wielesek[39] suggested, with symmetry arguments, that an S_σ correlated with the ground state of PI (the ring-opening radical that leads to BPI) while S_π correlates with an excited state of PI and thus *cannot be the primary precursor for ring opening*. Subsequent higher level treatments have supported this suggestion. They also agree with our suggestion that the S_π–S_σ energy separation is 10–15 kcal/mol.[40]

WEZ on Ring Opening. WEZ recognize only one variety of succinimidyl, the ground state, which is now recognized as π. They are in the position of ascribing ring opening to S_π.

Conclusion. We believe our evidence is conclusive for a succinimidyl radical that makes itself transparently evident, by additions to double bonds, and *does not* undergo ring opening. This succinimidyl shows different selectivities toward alkanes for H abstractions, toward alkenes for additions, and toward arenes for additions than does the succinimidyl radical that undergoes ring opening. We identify the ring opener as S_σ and non-ring-opener as S_π.

Registry No. NBS, 128-08-5; $BrCCl_3$, 75-62-7; $CH_2{=}CCl_2$, 75-35-4; *N*-(2-bromo-2-methyl-1-propyl)succinimide, 85925-70-8; 1-bromo-2-chloro-2-methylpropane, 10601-61-3; 2-bromo-1-chloro-2-methylpropane, 2074-80-8; 1-bromo-2,2-dichloropropane, 85925-71-9; 2-bromo-1,2-dichloropropane, 17759-88-5; β-bromopropionyl isocyanate, 18926-24-4; succinimidyl radical, 24344-83-0; neopentane, 463-82-1; *tert*-butyl chloride, 507-20-0; 2,2-dichloropropane, 594-20-7; butane, 106-97-8; 1-bromobutane, 109-65-9; isobutane, 75-28-5; 3,3-dimethyl-1-butene, 558-37-2; isobutylene, 115-11-7; 1,3-butadiene, 106-99-0; methylene chloride, 75-09-2; chloroform, 67-66-3; hydrogen, 1333-74-0; deuterium, 7782-39-0.

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

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

(34) Lessard, J.; Mondon, M.; Touchard, D. *Can. J. Chem.* **1981**, *59*, 431 and references therein.

(35) Sutcliffe, R.; Griller, D.; Lessard, J.; Ingold, K. U. *J. Am. Chem. Soc.* **1981**, *103*, 624. See also: Teeninga, H. Ph.D. Thesis, University of Groningen, 1983.

(36) Johnson, R. A.; Greene, F. D. *J. Org. Chem.* **1975**, *40*, 2186, 2192.

(37) Joseph, T. C.; Tam, J. N. S.; Kitadani, M.; Chow, Y. L. *Can. J. Chem.* **1976**, *54*, 3517.

(38) Lund, A.; Samskog, P. O.; Eberson, L.; Lunell, S. *J. Phys. Chem.* **1982**, *86*, 2458.

(39) Koenig, T.; Wielesek, A. *Tetrahedron Lett.* **1975**, 2007.

(40) Apeloig, Y.; Schreiber, R. *J. Am. Chem. Soc.* **1980**, *102*, 6144. Dewar, M. J. S.; Pakiari, A. H.; Pierini, A. B. *J. Am. Chem. Soc.* **1982**, *104*, 3242.