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Ground- and Excited-State Succinimidyl Radicals in Chain Reactions: A Reexamination

Philip S. Skell,* Ulrich Lüning, Douglas S. McBain, and James M. Tanko

Contribution from the Department of Chemistry, The Pennsylvania State University, University Park, Pennsylvania 16802.

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Abstract: The succinimidyl radical chemistry reported earlier and previously attributed to the σ state is reproduced, leaving unsettled only its assignment to the π and σ state. This chemistry, observed in the presence of small amounts of alkenes which scavenge bromine, includes the following: (1) additions to alkenes, (2) additions to arenes, (3) Cl-like substitution selectivities, and (4) ring-openings. The chemistry previously reported under the title "π" is neither as simple nor conclusive as thought earlier. As reported earlier, ring-opening is suppressed by inclusion of bromine, benzene, bromotrichloromethane, or larger amounts of alkenes. These observations indicate the presence of a different chain carrier, formerly labeled as S_π. We show now that the S_π explanation was not correct with addends benzene, bromotrichloromethane, and olefins, and we identify the specific competitive processes. Reactions in the presence of bromine still show evidence for a third hydrogen abstractor besides an imidyl radical and a bromine atom. At this time there is no unambiguous identification of this third chain intermediate.

Subsequent to the recognition of succinimidyl radical chemistry,[1,2] we reported evidence for the participation of two succinimidyl radicals, which we assigned to the π and σ states.[3,4] On reexamination, we now find that the evidence for the species we *labeled* "π" is not definitive and for the present we withdraw the conclusions based on that work. The experimental results which we attributed to a "σ" *succinimidyl radical*[5] are reproduced and stand without modification, *except* for the attribution of this chemistry to the σ state. Since there are doubts about the assignment of spectroscopic states, we propose to abandon such assignments and identify the chemistry formerly called "σ" as that of the succinimidyl radical; this is the key for the connection to our earlier published work. We suggest that until the matter is settled this intermediate *not* be identified with the spectroscopically designated σ state.

This paper describes the results of our re-examination of the chemistry we had described[3,4,6,7] with the title "π" *succinimidyl radical.*

Historical

For some 30 years following the Ziegler discovery[8] of allylic brominations (1942) with *N*-bromosuccinimide (NBS) in CCl_4, the chemistry of succinimidyl radical remained unrecognized despite numerous efforts toward that objective. Extensive explorations had led to the conclusion that NBS operated exclusively with a bromine atom chain.[9] Indeed, we employed a Br_2–NBS reagent system in our studies of β-bromine bridging in radicals to have bromine atom chains free of complications resulting from the presence of HBr; NBS scavenged the HBr and maintained constant Br_2 concentrations.[20] We began to explore succinimidyl radical chemistry only after repeated assertions that our scavenging of HBr was inadequate and that bromine atoms in the absence of HBr showed low selectivities, similar to chlorine atoms.[10] These claims instigated investigations which led to the simultaneous recognitions in our laboratory[1] and Traynham's[2] that the succinimidyl radical was the species with selectivities similar to those of chlorine atoms.

A critical factor[1] in the success of the Ziegler method for allylic brominations was the use of CCl_4,[8] a medium in which NBS has low solubility ($\sim 10^{-3}$ M), thus decreasing the participation of a chain reaction involving the imidyl radical. The following experimental requirements make imidyl chemistry accessible from their N-bromo compounds in a form uncontaminated by competing chain processes:[3,4] (1) maintain higher concentrations of *N*-bromo reactants by use of solvents such as methylene chloride, chloroform, or acetonitrile, and (2) scavenge Br_2 with alkenes. Both of these conditions help to suppress bromine atom chains relative to the imidyl chains.

In contrast to NBS reactions in CCl_4, in these "better" solvents chemistry of a new carrier became accessible: additions to benzene, additions to alkenes, ring-openings and hydrogen abstractions with low selectivities, reminiscent of chlorine atom behavior.[4] To demonstrate this was not attributable to bromine atoms, the early studies of this new species focused on inter- and intramolecular competitions: (1) cyclopentane–cyclohexane,[2] (2) methylene chloride–neopentane,[1] and (3) *n*-butane.[4,6,7] These selectivities were similar to those of Cl· and distinctively different from those of Br·. This new chemistry was attributed to succinimidyl radical as the principal chain carrier.[1,2]

These results are reproducibly observed in the presence of small amounts of various alkenes. This had led to the conclusion that scavenging of Br_2 (and Br·) was the key to observing succinimidyl chemistry.[4,5] Previously, the only chemistry associated with succinimidyl radical was a characteristic ring-opening reaction, invoked to explain the isomerization of NBS to β-bromopropionyl isocyanate (BPI),[11] some radical scavenging, and ESR experiments.[12,13] INDO calculations and symmetry considerations predicted that the ground state of the succinimidyl radical was π, the excited state σ, and that ring-opening would occur only from the σ state.[14]

Subsequently it was reported that in the presence of Br_2 not only was this chlorine-like behavior and ring-opening largely eliminated *but a new pattern of substitution selectivities, which also were distinctly different from that of Br·*, were observed.[3,4] This led us to the conclusion that a second variety of succinimidyl

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radical was involved, which we attributed to the π state; the chlorine-like behavior we attributed to the σ state. The same "π" selectivities were also reported to be observed under other circumstances *in the presence of bromine-scavenging* olefins, thus giving support to the hypothesis of two succinimidyl radicals.[6,7] It is remarkable that until quite recently, three independent groups of investigators had agreed that two succinimidyl-derived chain carriers were involved,[15,16] in addition to the Br· carrier; *there was only objection to our assignment of the π and σ structures to these two species.* We now raise questions regarding the validity of all of these results which led to the conclusion that two types of succinimidyl radicals had been recognized.

Walling,[15] and then Tanner and Walling,[23] have focussed their attention exclusively on the π–σ part of this development. Their attack on the π–σ controversy has been a re-examination of our experiments (which now admittedly were not definitive), reporting minor differences between us. Their only extension[23bcd] into an area not reported by us was their examination of Traynham's cyclopentane/cyclohexane competitions[32] which Tr had shown to have an unexpected factor of 10 difference in selectivity for Br· and S·. However, this system is surely unsuitable for attempting to distinguish between S_σ and S_π, for two reasons: (a) the system would not be expected to show different selectivities with such similar substrates,[23c] and (b) it had been demonstrated earlier that NBS/Br_2 operates exclusively on secondary hydrogens with a bromine atom chain.[20] Thus, although we use primary/secondary and primary/tertiary competitions for studies in the presence of bromine scavengers, the examination of the NBS/Br_2 system used neopentane/methylene chloride competitions since bromine atom chains are slow with these substrates. On the basis of such experiments, we now conclude there is no satisfactory experimental support for our π–σ hypothesis in the imidyl systems.[33]

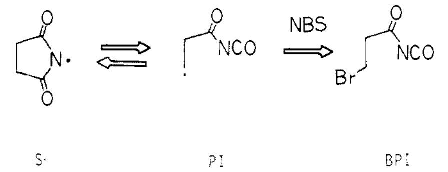
The observation that Br_2 suppressed ring-opening indicated reaction conditions where a new chain carrier might be found; *when BPI formation is suppressed, other chain carriers must be involved, and it was toward the identification of such species that we had turned our attention.* Our only concern with BPI yields had been to serve as a guide to the presence of other chain carriers.

The Walling and Tanner papers[15,23] have focussed heavily on the relationship of ring-opening to substitution selectivity. Our data, and theirs, support our original claims of suppression of ring-opening in the presence of Br_2, benzene, or $BrCCl_3$; for the main they confirm our observations. For a quantitative treatment they developed an equation relating yields of ring-opening product and substitution selectivity, which is discussed in Appendix 2; the equation fails completely for NBS/Br_2 in the crucial area of higher Br_2 concentrations.

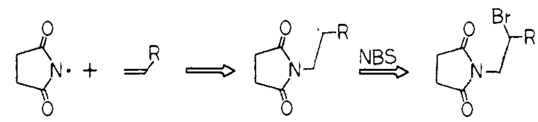
Review of Reconfirmed Succinimidyl Chemistry

The major focus has been on studies of *N*-bromosuccinimide (NBS) in methylene chloride solvent (with some studies of *N*-chlorosuccinimide (NCS)), in the presence of small amounts of alkenes which scavenge bromine. These reactions illustrate the unusual behavior of imidyl radicals.

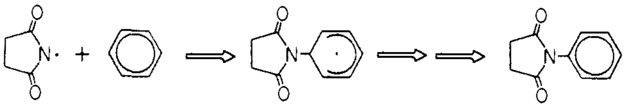
Ring-opening to β-bromopropionyl isocyanate (BPI) is an important reaction channel with NBS, one which is not observed with NCS. This was related to reversible ring-opening (confirmed with deuterium labeling) and the slower rate of trapping of PI by NCS.[17,5]



(2) At high concentrations of alkene, 1:1 addition products are produced in good yield with corresponding diminution of BPI yield.[18,5]



(3) Additions to benzene and other arenes occur with approximately the same rate constant as the additions to alkenes.[18,6]



(4) Substitution reactions occur with selectivities similar to those of Cl·.[4] For example, in neopentane/methylene chloride competitions[5] the relative rate on a per hydrogen basis (r) is 17 for S·, 50 for Cl·,[31] and 0.03–0.07 for Br·.[15,23,30] Abstraction of hydrogen from neopentane occurs at a ratio 0.16× the rate of addition of S· to *tert*-butylethylene,[5] a relative rate closely similar to the value of 0.21 shown by Cl·.[19]

Reexamination of Evidence for "π" Imidyl Radicals

The addition reactions (to alkenes and arenes) are especially important in identifying the chain carrier as an imidyl radical, since the imidyl fragment becomes a part of the product molecule. This is not the case in substitution reactions where the origin of a product such as succinimide is not unambiguously recognizable: for example, it may be formed in the nonradical reaction of NBS with HBr.[20]

The invocation of a second variety of imidyl radical was based wholly on substitution chemistry, thus providing only indirect evidence for the involvement of an imidyl radical. Substitution selectivities distinctly different from those of Br· and the imidyl intermediate obtained in the presence of alkenes were the basis of the conclusion that a second imidyl radical was involved.[3,4,6,7] Ultimately our suspicions were aroused by an inability to observe any addition chemistry that required this postulated second variety (π) of the imidyl radical. This failure to find additions to alkenes was suspicious despite well-documented observations that substituted amidyl radicals, $RCO\dot{N}R'$, have a π ground state and do not add to alkenes.[28]

The conditions for attaining the selectivities which had been attributed to a "π" succinimidyl were the following: (1) *NBS and Br_2* in CH_2Cl_2 solvent, applicable only in cases where the substrate C–H bonds react slowly with Br·, such as neopentane, methylene chloride, *tert*-butyl chloride, and 2,2-dichloropropane; (2) NBS and alkene *in the presence of benzene*, in CH_2Cl_2 solvent; and (*3*) NBS and alkene *in the presence of $BrCCl_3$*, in CH_2Cl_2 solvent. Under each of these conditions it was claimed that (1) the amount of ring-opening was greatly reduced[3-7] (now reconfirmed) and (2) identical substitution selectivities were observed in all cases for which the three methods could be employed in competition reactions[7] (now *not* confirmed). Since the latter evidence was the foundation of the hypothesis that a second imidyl radical was generated under these three sets of conditions, that conclusion has lost its support. As is shown below, the yields of substitution products by methods 2 and 3 were unusually small and the agreement among the methods fortuitous. However, the reactions

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Table I. Photoinitiated Bromination of *n*-Butane with NBS in the Presence of Benzene or $BrCCl_3$ at 12 °C

expt no.[a]	additive[b]	NBS converted (%)	BuBr (% of conversion of NBS)	$k(2°/1°)_H$[c]
1		100	65	4.6
2		100	52	4.7
3	0.6, C_6H_6	36	14	4.9
4	1.2, C_6H_6	58	7	~5
5	3.2, C_6H_6	~90	3	5.5
6	5.6, C_6H_6	~50	2	7.7
7	5.6, C_6H_6	11	3	10.1
8	11.3, C_6H_6	38	2	9.4
9	11.3, C_6H_6	17	3	8.0
10	0.6, $CBrCl_3$[d]	37	40	5.1
11	1.2, $CBrCl_3$[d]	25	48	5.8
12	4.0, $CBrCl_3$[d]	10	50	7.2

[a] 1-2 mmol of NBS, 1-2 mol of $H_2C{=}CH_2$. [b] mol/L. [c] On a per hydrogen basis. [d] No yellow color appearance during reaction.

in the presence of Br_2 remain an enigma; these reactions have proven to be complex in a manner not yet resolved.

NBS in the Presence of Benzene

The effect of the presence of benzene on NBS chemistry was first examined to find the concentration of benzene which would largely eliminate the ring-opening reaction that had been identified with S_σ chemistry. Since this is accomplished with ~2 M benzene,[6] this concentration was adopted as the recipe with which to explore the substitution selectivities that had been attributed to the π state.[7] We conclude now that the selectivities obtained in this manner gave an accidental agreement with the other methods as a consequence of choosing this recipe.

In our preliminary report on reactions of NBS with arenes,[18] we indicated a product ratio of *N*-phenylsuccinimide to succinimide to dibromoalkane (from addition of Br_2 to the alkene) of 1:1:1. In subsequent work, examining substitution reactions with use of the 2 M benzene recipe, we found in a number of instances a 1:2:1 stoichiometry,[6,7] consistent with the proposal that S_σ reacted with benzene to make a cyclohexadienyl radical (SC·) which then reacted with NBS to make S_π. This stoichiometry was the basis for one of the crucial arguments in favor of the "π" hypothesis (with the further requirement that S_π does *not* add to benzene, see Scheme V in ref 6).

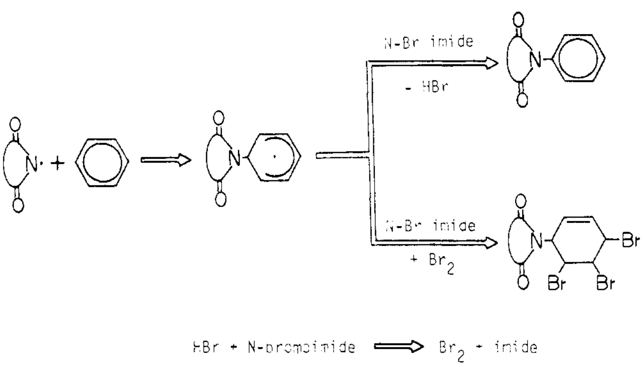
For NBS and 33DMNBG[21] the stoichiometry of the formation of imide, *N*-phenyl imide, and dibromoalkane was reinvestigated at 70 °C. At this temperature clean 1:1:1 stoichiometry is found. These observations severely contradict the claim that a second variety of imidyl radical is produced in the presence of benzene, one that does not add to benzene.

However, at 15 °C these systems become more complex.[21] At this temperature less *N*-phenyl imide than imide is formed and the NMR spectra show additional peaks which probably belong to *N*-(tribromocyclohexenyl) imides reported earlier by Chow and co-workers.[22]

These findings are not in accord with the "π–σ" hypothesis.

Finally, to exclude the possibility that a small amount of a second imidyl radical accounts for the "non-σ" selectivities, the system was investigated to redetermine the substitution selectivities in the presence of benzene.

Scheme I



With *n*-butane as substrate, in methylene chloride (no benzene present) high yields of bromobutanes (BuBr) can be achieved with NBS with small amounts of alkene. The only side reaction is the formation of BPI (Tables I and II). In the presence of benzene, however, the yields of BuBr drop considerably with increasing benzene concentration. Only 2–3% of the converted NBS lead to BuBr in reactions where the benzene concentration is 3 M or higher (Table I). The major products are the *N*-phenyl imide and the dibromoalkane, generated from Br_2 scavenging by the alkene, and minor amounts of *N*-(tribromocyclohexenyl)succinimide, as Chow reported,[22] and BPI. Although the yields of BuBr are very low (which means large errors in determining selectivity), the *r* values are close to the value obtained in CH_2Cl_2 in the absence of benzene. In Table II experiments are listed for which all the reaction products have been determined.

The unavoidable conclusion is that the major radical chain reaction of NBS in the presence of benzene is the simple addition to the benzene as shown in Scheme I and that substitutions on alkanes compete poorly. Furthermore, these low yield substitution reactions occur with the same selectivity as in the absence of benzene, thus providing evidence that the same imidyl radical is responsible for the substitution reactions in the presence or in the absence of benzene.

Earlier it was recognized that the ring-opening reaction was much faster for the 2,2-dimethylsuccinimidyl radical than for the unsubstituted succinimidyl. Consistent with that conclusion is the finding[21] that in benzene (neat) at 70 °C ring-opening of the succinimidyl radical is largely suppressed (~1% BPI), but ring-opening of 2,2-dimethylsuccinimidyl radical is the major reaction (~70% Me_2BPI). These results indicate the involvement of a single variety of imidyl radical which is distributed between the reaction channels for the unimolecular ring-opening and the addition to benzene.

Reactions of NBS in the Presence of $BrCCl_3$

Bromotrichloromethane at 4 M concentration in methylene chloride, and in the presence of small amounts of vinylidene chloride, is a system in which NBS reacts with very little ring-opening;[7] this system had been employed to examine the substitution selectivities which we believed were attributable to S_π. Re-examination of this system *fails to support the original claims* that a new unique selectivity was observed for the hydrogen-abstraction in substitution reactions, which was ascribed to S_π.[7]

The olefin component is rapidly depleted in this system, presumably by addition of $BrCCl_3$, and subsequently yellow color is evident from formation of bromine. Consequently, only results obtained prior to the development of the yellow bromine color are significant in probing this system. Tanner's claim[23d] that BPI is

Table II. Photoinitiated Bromination of *n*-Butane by NBS in the Presence of Benzene or $BrCCl_3$ at 12 °C

expt no.	NBS[a]	$H_2C{=}CH_2$[a]	$n\text{-}C_4H_{10}$[a]	[additive][b]	irradiation time,[c] min	% NBS converted	BuBr[a]	S–Ph[a]	SH[a]	tri-bromide[a]	BPI or[a,d] BPA	$r(2°/1°)$[e]
13	2.16	0.56	19.3		20	100	1.55		1.54		0.60	4.6
14	1.31	3.53	16.8	1.0 (C_6H_6)	80	75	0.096	0.17	0.45	0.10	0.26	5.1
15	1.27	1.65	16.9	3.2 (C_6H_6)	150	100	0.04	0.43	0.51	0.15	0.14	5.8
16	2.64	0.63[f]	9.7	3.8 ($BrCCl_3$[g])	60	<3	0.005		~0.05			4.4

[a] mmol, in 5 mL (78 mmol) of CH_2Cl_2. [b] mol/L. [c] UV irradiation with a 400-W medium-pressure mercury are through Pyrex from 5-cm distance. [d] Analyzed either as β-bromopropionyl isocynate (BPI) or, after hydrolysis, as β-bromopropionamide (BPA). [e] (2°/1°) × 1.5. [f] $CH_2{=}CCl_2$. [g] No yellow color appeared during reaction.

produced in the presence of $BrCCl_3$ may be a consequence of operating beyond the scavenging capacity of the alkene. Although substitution yields are small during this period, the selectivities are the same as obtained in the absence of bromotrichloromethane, contradicting our earlier conclusions. Tables I and II shows these selectivities for butane.

Reactions carried out to larger conversions, and thus partially in the presence of bromine, show larger 2°/1° selectivities, readily understandable as the consequence of a mixed chain with S· and Br· carriers. It was these values, which earlier were mistakenly cited[7] as evidence for the involvement of S_π in "$BrCCl_3$ moderated systems".

In these systems the participation of $\cdot CCl_3$ in substitutions appears to be unimportant. This is apparent from the failure to find $HCCl_3$, as also reported earlier,[6,7] among the products; chloroform survives these reaction conditions; it does not react when introduced into this system.

Bromine–NBS Systems

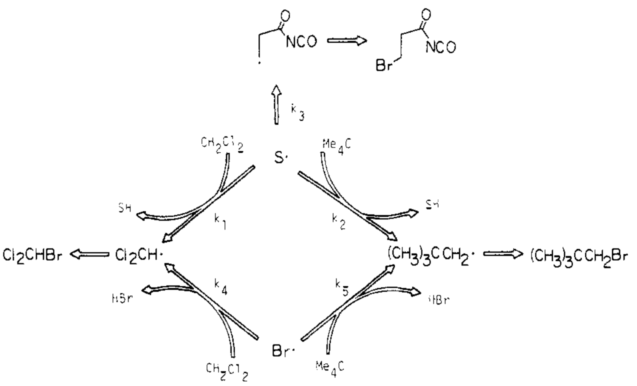
Early it was recognized that $\geq 10^{-2}$ M concentrations of Br_2 largely eliminated the ring-opening reaction, suggesting to us at the time that a second imidyl radical (S_π) was operating under these conditions. This hypothesis was tested by studying competitive substitution reactions utilizing substrates with low reactivities toward Br·, such as neopentane, methylene chloride, 2,2-dichloropropane, and *tert*-butyl chloride,[3,4,7]

With the low-reactivity substrates, a selectivity different from that of either a bromine atom or a succinimidyl radical was observed.[7] This unique selectivity, in conjunction with the supression of the ring-opening reaction,[5,7] provided part of the foundation for the π–σ hypothesis.

Initially, the NBS–Br_2 system seemed to hold promise of being simple. This assessment has proven to be incorrect. In our hands, and apparently others,[15] nonreproducibility of selectivities has been a persistent problem. We have succeeded in identifying several factors which contribute to this irreproducibility and corrected them. With this reagent (22DMNBS/Br_2) a selectivity is found different from that of S· or Br· (see Table V). Although we do not at present completely understand the system, it is nonetheless important to report the shortcomings of our earlier claim that this NBS–Br_2 reagent carried out substitutions on low-reactivity substrates with the "π" succinimidyl radical. The evidence refutes unambiguously the possibility that a mixture of bromine atom and succinimidyl radical chains alone suffices to explain the unique selectivity observed with this reagent.

In neopentane/methylene chloride competitions with the NBS/Br_2 reagent, we find the following experimental considerations to be crucial to the observation of a reproducible per hydrogen relative reactivity (r): (1) The preparation of standard solutions of Br_2 in CH_2Cl_2 for use in these experiments has proven to be a major source of irreproducibility. Despite the obvious precaution of protecting these solutions from light, within a time period of less than 24 h, a substantial quantity of $BrCHCl_2$ is formed: Adding Br_2 directly to the reaction mixture *immediately before* irradiation has proven to be a satisfactory procedure. (2) Since bromine, methylene chloride, and neopentane have appreciable vapor pressures, the results are complicated by concurrent gas phase bromine atom mediated reactions. This results in lowering the observed r value toward that of a bromine atom. This becomes particularly important if low-volatility inhibitors are present in the liquid phase. Shielding the gas phase with aluminum foil minimizes this complication. (3) Purity of neopentane plays a puzzling and important role. As received from the supplier (Matheson), the neopentane contains 0.35% butenes and 0.30% butane as the major contaminants. Purification by addition of Br_2 followed by reisolation of the neopentane increases the purity to 99.6%, through removal of the olefin contaminants. Extended photobromination of the neopentane, followed by reisolation, increases the purity to 99.99%, effectively eliminating all traces of olefin and butane. Each of these samples of neopentane produce different observed values of r. In our experiments, the 99.99% pure neopentane was used. (4) Trace quantities of water, introduced in a manner as innocent as pipetting methylene chloride, appear to have the effect of lowering the observed r value. We rigorously exclude water from our reactions through the use of anhydrous solvents, syringe techniques, inert atmosphere, etc.

Scheme II



These experiments were carried out with 2,2-dimethyl-*N*-bromosuccinimide (22DMNBS) instead of NBS for the following reasons: (1) 22DMNBS is more soluble in CH_2Cl_2. The reaction mixtures are homogeneous. (2) 22DMS· ring opens irreversibly[5] and at a rate faster[5] than that of S·. Consequently, conditions under which small amounts of ring-opened products are observed with NBS will produce substantially greater amounts of ring-opened products with 22DMNBS. (3) The ^1H NMR analyses of the product mixtures are simpler and more reliable with 22DMNBS. The ^1H NMR spectrum of 3-bromo-3-methylbutanoyl isocyanate, the ring-opened product of 22DMNBS, consists of two sharp singlets at δ 1.8 (6 H) and 3.0 (2 H). Thus, the detection limits for the isocyanate are lowered (singlet of 6 H instead of triplet of 2 H). Addition of water results in hydrolysis to the amide with δ 1.8 (6 H) and 2.7 (2 H).

Thus, 22DMNBS provides a simple, more sensitive probe for ascertaining the relative importance (or unimportance) of the ring-opening reaction under a variety of conditions.

In Me_4C/CH_2Cl_2 competitions, the selectivity observed with the NBS/Br_2 reagent is intermediate between that of Br· and S·. Thus, the issue of whether this unique selectivity reflects the intermediacy of a *third* H-abstracting species or is merely the result of concurrent S· and Br· chains must be addressed. If indeed a mixed S·/Br· chain (Scheme II) is operating, then the properties of the "mixed" system must be consistent with *all* the known chemistry of S· and Br·, not simply substitution selectivities. The ring-opening reaction of S· provides the key to resolving this issue.

In this section, we report results regarding the chemistry of 22DMS·, particularly H-abstraction from Me_4C or CH_2Cl_2 relative to ring-opening. We demonstrate that the chemistry of 22DMNBS/Br_2 is *inconsistent* with the participation of only concurrent S·/Br· chains. Specifically, *the observed yields of neopentyl bromide are higher and of ring-opened product are lower than those predicted by concurrent S·/Br· chains only.*

To characterize 22DMS·, competition experiments utilizing 22DMNBS in the presence of ethylene were performed so as to determine the rate constant for ring-opening, relative to H-abstraction from Me_4C and CH_2Cl_2 (Table III). It is readily apparent that for 22DMS, *ring-opening* rather than H-abstraction is the predominant reaction pathway (Scheme III). Utilizing the data of Table III, a plot of the (yield neopentyl bromide)/(yield isocyanate) vs. neopentane concentration (Figure 1) produces a straight line of slope k_2/k_3. From these results, k_2/k_3 = 0.0022 M^{-1}, and within the detection limit, k_1/k_3 is zero ($\leq$0.00004 M^{-1}). For unsubstituted succinimidyl radical, k_2/k_3 = 0.088.[5] Assuming k_2 is the same for both radicals, then it appears that 22DMS· rings open at a rate approximately 40× that of S· at 12 °C.

The 22DMNBS/Br_2 system was studied as a function of Br_2 concentration. In Table IV, we report results of neopentane/methylene chloride competitions. It is immediately evident that at Br_2 concentrations >0.05 M, the observed selectivity (3.0–7.5) falls between that of a bromine atom (<0.1) and a succinimidyl

Scheme III

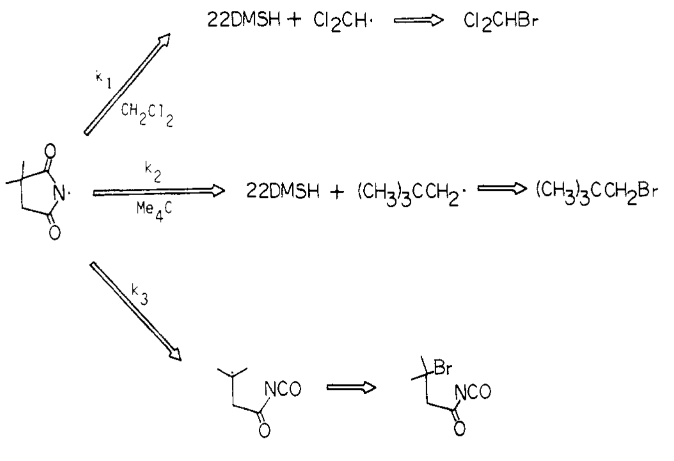


Table III. Neopentane/Methylene Chloride Competitions with 2,2-Dimethylsuccinimidyl Radical[a]

$[Me_4C]$, M	product yields (%)[b] $CHBrCl_2$	Me_3CCH_2Br (A)	$BrMe_2CCH_2C(O)$-NCO (B)	A/B
0.74	0 (±0.04)	0.14	99.0	1.39×10^{-3}
1.61	0 (±0.06)	0.38	98.6	3.82×10^{-3}
2.8	0 (± 0.04)	0.59	97.8	6.05×10^{-3}

[a] For all experiments, [22DMNBS] = 0.105 (±0.002) M, $T = 12 \pm 2$ °C. Br_2 and Br· scavenged with $C_2H_4$1 (C_2H_4/22DMNBS, mol ratio 0.7–0.8). Reactions photoinitiated with 400-W medium-pressure mercury arc lamp thru Pyrex at a distance of ca. 10 cm from reactants. Reaction times: 20 min. [b] Yields based upon starting 22DMNBS.

radical (~17). For this reason it might be reasonable to postulate that this intermediate selectivity implies the operation of only S· and Br· chains. However, such a hypothesis suffers from its inability to reconcile the observed chemistry with all known properties of S· and Br·. As will be demonstrated for the 22DMNBS/Br_2 system, the high yields of substitution products and low yields of ring-opened product are inconsistent with the assumption that 22DMS· and Br· are the only H-abstracting species.

Table V summarizes the yields of neopentyl bromide under the condition of a pure Br· chain (<9%) and a pure 22DMS· chain (<1%). With the 22DMNBS/Br_2 reagent, 30–60% yields of neopentyl bromide are obtained when $[Br_2] > 0.05$ M. It is grossly unreasonable to suppose that a mixed S·/Br· chain produces neopentyl bromide in greater yield than either chain alone.

If one assumes an upper limit of 0.1 for the *r* value of Br·, then a Br· chain (neopentane and methylene chloride concentrations 1 and 15.6 M, respectively) would produce neopentyl bromide and $CHBrCl_2$ in a ratio of 0.038:1. Thus, a *pure* Br· chain run to 100% conversion should produce neopentyl bromide in a yield ≤3.7%. Yet the 22DMNBS/Br_2 reagent produces neopentyl bromide in *30–60%* yields.

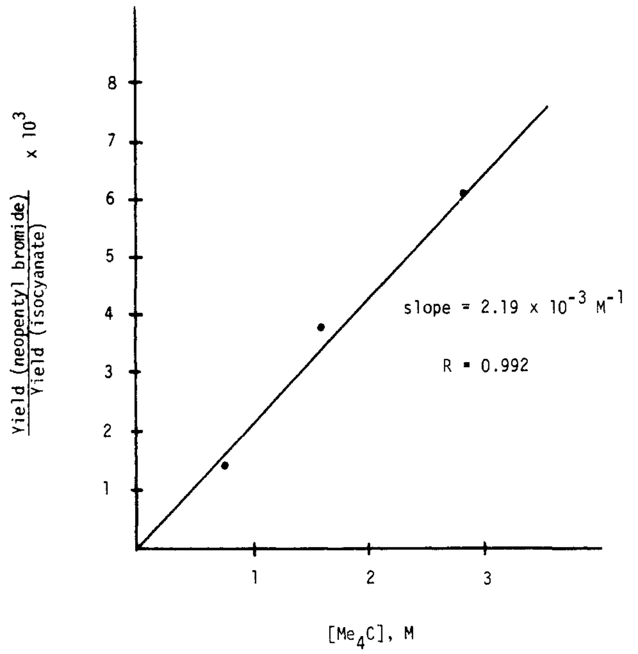


Figure 1. Ratio of neopentyl bromide to isocyanate formed in reactions of 22DMNBS with neopentane in the presence of C_2H_4.

Further, the yield of ring-opened product is entirely too low to involve any significant contribution of a 22DMS· chain. For 22DMS·, the relative ratio of ring-opened product to neopentyl bromide (at 1 M neopentane) is 450:1. *If the excess neopentyl bromide* produced by 22DMNBS/Br_2 *were attributed to 22DMS·*, ridiculous yields of ring-opened product in the range 12000–32000% would be required!

This relationship between the yield of substitution products and the predicted yield of ring-opened product is described quantitatively (and in more detail) in Appendix 1. One point emerges quite clearly: While the S·/Br· hypothesis would *appear* to explain observations of some of the intermediate *r* values in the 22DMNBS/Br_2 or NBS/Br_2 systems, it completely fails to reconcile known succinimidyl radical chemistry (particularly intramolecular ring-opening) with these observations. Since the intrinsic properties of S· cannot change, one is inevitably forced to conclude that a third intermediate is operating in the NBS/Br_2 system.

Appendix 2 details a quantitative treatment of the subject based upon the equation of Tanner and Walling.[23] There is agreement that with bromine scavengers present the chain carrier is S·. In the presence of insufficient alkene, or low Br_2 concentrations, it is reasonable to have a mixture of S· and Br· chains operating. The crucial question is what happens in the presence of Br_2 concentrations in excess of 0.05 M. It is exactly in this region that the equation makes grossly incorrect predictions for the behavior of this system. Applied to 22DMNBS or NBS itself,

Table IV. Results of Neopentane/Methylene Chloride Competitions for Intermediates in the 22DMNBS/Br_2 System[a]

$[Br_2]$, M	$[Me_4C]$, M	time, min	yields of products[b] and recovered reactants (%) $CHBrCl_2$	Me_3CCH_2Br	22DMSH	22DMNBS	isocyanate[c]	Br_2[d]	*r*[e]	*Y*, calcd[f] (%)	%[isocyanate][g] calcd
0.016	1.09	20	14.4	1.66	29.1	59.9	3.1	53	0.28	95.5	6.4×10^2
0.051	0.90	30	32.3	45.2	67.7	2.8	≤0.9	93	4.1	99.7	2.3×10^4
0.051	0.98	20	26.0	39.1	59.0	9.3	≤6.5	90	4.0	99.6	1.8×10^4
0.098	0.88	24	15.8	35.7	55.3	29.2	≤0.4	95	6.7	99.7	1.8×10^4
0.20	0.63	20	12.4	20.5	35.8	57.1	≤0.5	97.0	6.8	99.8	1.5×10^4
0.39	0.92	20	11.7	30.8	45.2	46.2	≤0.4	93.8	7.5	99.7	1.5×10^4
0.78	0.85	20	6.44	7.35	16.2	78.3	≤0.3	79.2	3.5	99.6	3.9×10^3
1.2	0.80	20	5.45	5.09	12.3	83.9	≤0.2	87.5	3.0	99.6	2.9×10^3

[a] in all experiments, $[22DMNBS]_i = 0.10 \pm 0.01$ M in CH_2Cl_2, $T = 12 \pm 2$ °C, and initiation is accomplished with a 400-W medium-pressure mercury arc lamp at a distance of 5 cm through 2 layers of Pyrex. [b] Product yields based upon starting 22DMNBS. [c] $BrC(CH_3)_2CH_2C(O)NCO$. [d] Based upon initial bromine. Detected by GLC as the addition product of *tert*-butylethylene, added after irradiation. [e] Observed selectivity, r = [(yield neopentyl bromide)/(yield bromodichloromethane)] (mmol CH_2Cl_2/mmol Me_4C) (1/6). [f] Isocyanate yield calculated (assuming mixed S·/Br· chains) from the observed *r* value with the Tanner/Walling equation. See Appendix 2. [g] Isocyanate yield calculated (assuming mixed S·/Br· chains) from the yield of substitution products. See Appendix 1.

Table V. Yields of Neopentyl Bromide in Neopentane/Methylene Chloride Competition Reactions for 22DMNBS/Br_2 Mixtures

reactant concn, M				neopentyl bromide yield,
22DMNBS	Br_2	Me_4C	r_{obsd}[a]	%
22DMNBS/C_2H_4 Scavenger: 22DMS·Chain[b]				
0.1	0	0.78–2.8	*c*	<1
Br_2 Alone: Br· Chain[d]				
0	0.1–7	0.7–4	0.03–0.1[30]	0.6–9[15,23]
22DMNBS/Br_2[e]				
0.1	0.016	1.09	0.28	4.1
0.1	0.051	0.90	4.1	47
0.1	0.051	0.98	4.0	43
0.1	0.098	0.88	6.7	50
0.1	0.20	.63	6.8	48
0.1	0.39	0.92	7.5	57
0.1	0.78	0.85	3.5	34
0.1	1.2	0.80	3.0	32

[a] r_{obsd} = [(yield Me_3CCH_2Br)/(yield $CHBrCl_2$)] ([CH_2Cl_2]/[Me_4Cl]) (1/6). [b] Yield based on 22DMNBS. [c] $BrCHCl_2$ yield below detection limit; see Table III. [d] Yield based on Br_2. [e] Yield based on 22DMNBS; CH_2Cl_2 solvent. Any HBr produced will react with 22DMNBS to make 22DMSH and regenerate Br_2; see Table IV.

the same conclusion is reached: The chemistry of these systems in the presence of Br_2 is clearly *not* ascribable to a mixture of S· and Br· chains solely.

Thus, the evidence leads one to postulate that a *third* H-abstracting species is involved, that it possesses a unique selectivity, and if its structure includes a succinimidyl derived moiety, that it does not undergo ring-opening under these conditions. The identity of this third species is unclear at this point. There are two obvious possibilities: (1) a second type of succinimidyl radical or (2) a complex of composition (SBr_2·). We believe the currently available body of data is insufficient to reach any definitive conclusion.

Theoretical Treatments. The Dilemma

The only definitive spectroscopy in the field is an ESR spectrum, reported for succinimidyl, obtained from an X-irradiated crystal of succinimide. The spectrum indicated a π assignment for what must be the ground state.[24] This conclusion is supported by large scale ab initio multireference CI calculations in a double-ζ AO basis set. The energy differences to the first excited σ state were calculated to be 5.1[25] and 11.7 kcal/mol.[26]

Two theoretical treatments have reached the conclusion that ring-opening in a π state would be much slower than in a σ state; one of these treatments is based on orbital symmetry considerations,[14] the other on calculations of activation energy by the MNDO method.[27]

It is worth noting at this time that a dilemma exists. If ring-opening is assigned as a ground-state property, then it is occurring from the π state which should *not* undergo this reaction on the basis of the orbital symmetry and MNDO/3 arguments; this would be an example of nonoperation of the type of stereoelectronic control which is generally assumed to operate for ring-opening reactions. If, on the other hand, the stereoelectronic rationale operates in this case, then one would conclude that the major part of the presently known imidyl chemistry is that of an excited state, σ, and that very few, if any, ground-state reaction properties are known at present.

Conclusion

Although the high-level theoretical calculations indicate low-lying electronic excited states for the succinimidyl radical, making it reasonable to anticipate generating both ground and excited states, the data available at this time indicate conclusively that in the case of imidyl radicals only one of these has been definitively recognized and studied in some depth.[33] At present it is not certain this is the ground state, although that is the most reasonable supposition despite the fact that the ring-opening reaction must be attributed to a π state in violation of stereoelectronic control requirements. The alternative is to attribute the known chemistry to an excited σ state.

Another hydrogen-abstracting agent is present in NBS/Br_2 systems which is a species other than Br·, S·, or any mixture of these two. There is no convincing evidence at present for the identity of this third species.

Experimental Part

General Information. ^1H NMR data were taken with a Varian EM360, Bruker WP-200, Bruker WH-360 instruments with a δ scale relative to hexamethyldisiloxane (δ 0.07). GC data were taken on Hewlett Packett 5790 FID and Hewlett Packett 5890 TCD instruments with DB-5 30 m × 0.25 mm column and Hewlett Packett 3390A integrator, with chlorobenzene as the internal standard.

Materials. NBS was recrystallized from water and dried extensively in vacuo. 22DMNBS and 33DMNBG were used as described, recrystallized from CH_2Cl_2 or $CHCl_3$ by adding pentane or carbon tetrachloride. CH_2Cl_2 was distilled from P_2O_5 through a 1 m Vigreux column and stored over 3 Å molecular sieves. The center cut showed no impurities (GLC). Benzene was Fisher, recrystallized twice, stored over 4 Å molecular sieves, with a purity of 99.998% (GLC). $CBrCl_3$ was distilled through a spinning band column, center cut >99.8%, 0.1% CBr_2Cl_2 (GLC). CH_2CCl_2 was from Aldrich, distilled prior to use. *n*-Butane was from Matheson, used without further purification. Ethene was from Matheson, research grade (>99.99%), used without further purification. Bromine, hexamethyldisiloxane, and chlorobenzene (HPLC grade) were all from Aldrich, used without further purification. *neo*-C_5H_{12} was from Matheson. Research grade neopentane (99.6%) was purified by the bromination of the major contaminants (butane and butenes). A neat sample of Me_4C and Br_2 (excess) in the presence of K_2CO_3 was irradiated overnight with a 275-W sunlamp. Unreacted Br_2 was quenched with corn oil (Mazola), and Me_4C was distilled through two −78 °C traps and collected at −196 °C. By this procedure, Me_4C of purity >99.99% (GLC) was obtained.

General Procedure. *N*-Bromo imide, solvent(s), and olefin reaction mixtures in a 30-mL Pyrex pressure tube (sealed with an O-ringed Telfon needle valve) were degassed by using a thaw-freeze-pump technique five times. The mixtures were irradiated with a 400-W medium-pressure mercury arc from a 5 cm distance through Pyrex in a water bath of 12 ± 1 °C for 30–180 min. Volatiles and nonvolatiles were separated by trap-to-trap vacuum distillation. The volatiles were analyzed by GLC and the nonvolatiles by NMR, using chlorobenzene and hexamethyldisiloxane, respectively, as internal standards.

22DMNBS/Br_2 Procedure. In a typical procedure, ca. 0.11 g of 22DMNBS was placed in a 30 mL pressure tube which was then evacuated (to remove traces of solvent and H_2O). After the tube was flushed

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(29) It should be noted that the predicted yields of isocyanate, calculated with eq 4 and 6, do not agree. The reason is that the yield of isocyanate in eq 4 is linked to the absolute yield of $CHBrCl_2$ whereas eq 6 relates observed *r* values to isocyanate yields without indicating absolute yields of substitution products. In the former case, it becomes clear that the high observed yields of substitution products would require % conversions *much* larger than 100%. The latter approach demonstrates that while intermediate *r* values (reconcilable as S·/Br· chains) are possible, the high yields of isocyanate (>98%) would require substitution yields <2%. Thus, the two approaches *are* essentially the same.

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(33) It might be tempting to generalize this conclusion to carboxy radicals. For this reason we emphasize here that the carboxy work was carried out in the temperature range −60 to −100 °C, a range in which Br· chains for substitution reactions are too slow to be observed. Consequently, in this instance two states of carboxy continue to provide the best basis for explaining the two types of carboxy selectivities observed. See: P. S. Skell and D. D. May, *J. Am. Chem. Soc.*, **105**, 3999 (1983).

with dry N_2, 5.0 mL of methylene chloride (distilled from P_2O_5 and stored over 3 Å molecular sieves under N_2 *or* Aldrich (99+%) gold label anhydrous under N_2) was added via syringe. After the tube was cooled to −196 °C and evacuated, Me_4C and bromine were condensed successively (via the vac-line).

After 5 freeze–pump–thaw degassing cycles, the flask was encased in aluminum foil such that only the solution phase would be exposed. After placement in a thermostat bath, the reaction mixture was irradiated with a 400-W medium-pressure mercury arc from a 5 cm distance through Pyrex.

Volatiles (Me_4C, CH_2Cl_2, Br_2, $CHBrCl_2$, Me_3CCH_2Br) were separated from nonvolatiles by trap-to-trap vacuum distillation. Br_2 was quenched with *tert*-butylethylene, the appropriate quantity of chlorobenzene (internal standard) added, and the resulting solution analyzed by GLC.

Nonvolatiles (22DMNBS, 22DMSH, 3-bromo-3-methylbutanoyl isocyanate) were analyzed by ^1H NMR vs. hexamethyldisiloxane (internal standard). In some instances, 20 μL of H_2O was added to the reaction mixture and the isocyanate analyzed as the corresponding amide.

Appendix 1. Attempts to Rationalize NBS/Br_2 Systems with Chain Carriers S· and Br· Alone

The application of a model based on S· and Br· as the only carriers, using the 22DMNBS/Br_2 system, leads to a grossly incorrect description.

As demonstrated in Me_4C/CH_2Cl_2 competitions with 22DMNBS under Br_2 scavenging conditions, 22DMS· ring opens at a rate sufficiently fast so as to preclude any H-abstraction from CH_2Cl_2 ($k_1/k_3 \simeq 0$, Scheme III). Thus, in the 22DMNBS/Br_2 system, H-abstraction from CH_2Cl_2 by 22DMS· can be excluded as a significant source of $CHBrCl_2$. If one supposes a mixed S·/Br· chain to explain these results, then clearly $CHBrCl_2$ would be formed *solely* by H-abstraction from CH_2Cl_2 by Br·. Since the per hydrogen selectivity of Br· in Me_4C/CH_2Cl_2 competitions (r_{Br}) is known, then the yield of neopentyl bromide formed by abstraction of a hydrogen from Me_4C by Br· (% $[Me_3CCH_2Br]_{Br}$) can be calculated from the observed $CHBrCl_2$ yield (% $[CHBrCl_2]$):

$$\% \, [Me_3CCH_2Br]_{Br} = 6r_{Br}\frac{[Me_4C]}{[CH_2Cl_2]}\% \, [CHBrCl_2] \qquad (1)$$

Assuming S· and Br· as the only H-abstracting species, then the yield of neopentyl bromide resulting from H-abstraction by S· from Me_4C (% $[Me_3CCH_2Br]_S$) is easily calculated by substracting % $[Me_3CCH_2Br]_{Br}$ from the total neopentyl bromide yield (% $[Me_3CCH_2Br]_{TOT}$):

$$\% \, [Me_3CCH_2Br]_S = \% \, [Me_3CCH_2Br]_{TOT} - \% \, [Me_3CCH_2Br]_{Br} \qquad (2)$$

Finally, H-abstraction from Me_4C by S· (k_2 in Scheme III) is in competition with the intramolecular ring-opening reaction (k_3 in Scheme III). Thus, the predicted yield of ring-opened product, % $[\text{isocyanate}]_{calcd}$, can be calculated:

$$\% \, [\text{isocyanate}]_{calcd} = \frac{1}{(k_2/k_3)[Me_4C]}\% \, [Me_3CCH_2Br] \qquad (3)$$

Thus, eq 1–3 define a relationship between the predicted isocyanate yield (based on the S·/Br· hypothesis) and the observed neopentyl bromide yield:

$$\% \, [\text{isocyanate}]_{calcd} = \frac{1}{(k_2/k_3)[Me_4C]}\left\{\% \, [Me_3CCH_2Br]_{TOT} - 6r_{Br}\frac{[Me_4C]}{[CH_2Cl_2]}\% \, [CHBrCl_2]\right\} \qquad (4)$$

Assuming r_{Br} has an upper limit of 0.1, and using the value of k_2/k_3 determined earlier, % $[\text{isocyanate}]_{calcd}$ can be determined for each experiment in Table IV. The results of these calculations appear as the final entry in Table IV.

The calculated yields of ring-opened product are not only inconsistent with experimental fact, they are beyond reason! This interpretation is seriously flawed, and the flaw is attempting to explain the results of Table IV on the basis of concurrent S·/Br· chains.

Appendix 2

To test the hypothesis that mixtures of S· and Br· suffice to explain the known chemistry of the NBS systems, Tanner and Walling have developed a quantitative treatment which relates the amount of ring-opening and selectivity in substitution reactions.

The observed substitution selectivity (r_{obsd}) is calculated from the product ratios:

$$r_{obsd} = \frac{\text{yield } Me_3CCH_2Br}{\text{yield } CHBrCl_2}\frac{[CH_2Cl_2]}{[Me_4C]}\frac{1}{6} \qquad (5)$$

The S·/Br· hypothesis attributes r values falling between those of S· and Br· to mixtures of the two, the fraction of the reactions attributable to S· and Br· being calculable from the observed value of r. A test of the validity of this hypothesis can be made by comparison of the calculated and predicted yields Y of a third product, the BPI.

The yield of ring-opened product (Y) depends on the amount of S·. We thank Professors Tanner and Walling for bringing to our attention their derivation of the relationship between these quantities:

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

where

$$Q = (k_5/k_4)[Me_4C] + [CH_2Cl_2] \qquad (7)$$

$$1/Y_s = (k_2/k_3)[Me_4C] + (k_1/k_3)[CH_2Cl_2] + 1 \qquad (8)$$

When we apply this relationship to our data (setting $k_1/k_3 = 0 \text{ M}^{-1}$, $k_2/k_3 = 0.0022 \text{ M}^{-1}$, and $k_5/k_4 = 6 \times 0.1 = 0.6$) and compare the predicted yield of ring-opened product (Y,calcd) to that actually observed (see Table IV), it becomes clear that the S·/Br· hypothesis does not predict correctly the yields of ring-opened product for the 22DMNBS/Br_2 system.[29]

When applied to their data on the NBS/Br_2 system, Walling and Tanner have also found evidence implying the existence of a third chain-carrying species in some experiments, although the significance to this conclusion is understated.

The 22DMNBS/Br_2 system clearly defines the limiting conditions for the observation of this phenomenon, which can only reasonably be ascribed to a third H-abstracting species.