relearn how to prepare all the simple functionalized molecules that are considered trivial by current standards. However, progress in the past few years has indeed been impressive, and methodology is hopefully now firmly footed on the path to this goal. The words of Winston Churchill[32] seem particularly appropriate at this time:

"This is not the end···it is not even the beginning of the end···but, it is, perhaps, the end of the beginning."

Ground-State and Excited-State Chemistry of Succinimidoyl Radical and Its Congeners

PHILIP S. SKELL* and JAMES C. DAY

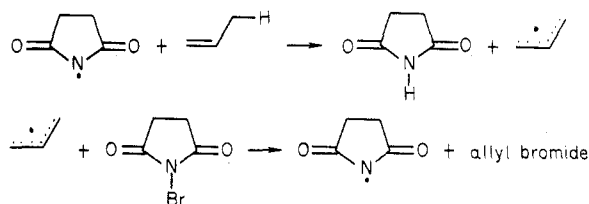*Department of Chemistry, The Pennsylvania State University, University Park, Pennsylvania 16802*
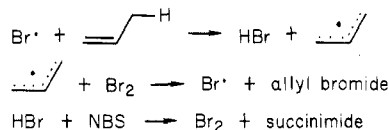
Prior to recent work, succinimidoyl radical chemistry was virtually unknown, despite a number of serious efforts. This once elusive radical system is now accessible, and the study of its reactions has yielded a number of surprises. The radical is unexpectedly reactive (early thinking suggested the opposite) in hydrogen abstractions and additions to double bonds and arenes. Further surprises resulted from the recognition that two succinimidoyl radicals were being produced, radicals with quite distinctive properties. Also, some interesting features along the way produced such questions as (1) when does a reaction take the less exothermic of two pathways and (2) are all structures contributors to a resonance hybrid structure?

Interest in the succinimidoyl radical can be traced to the recognition by Karl Ziegler and co-workers that *N*-bromosuccinimide (NBS) is a highly specific reagent for bromination of olefins at allylic positions. One feature of this surprising reaction was the requirement that carbon tetrachloride be used as the solvent, a feature which was accepted by the scientific community. Indeed this is a necessary part of the procedure, but we could not find anywhere in the abundant literature a reason for this extraordinary requirement.

Succinimidoyl radical began to receive attention when the radical-chain characteristics of the Ziegler bromination reaction[1] became apparent.[2] In the form of the Bloomfield mechanism,[2a] with succinimidoyl radical as the hydrogen-abstracting component of the chain sequence, it enjoyed only a short popularity. It yielded

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James C. Day was born in New Britain, Conn., in 1944, received his B.S. degree from the University of Hartford, and the Ph.D. from Case Western Reserve University (with L. Friedman). After postdoctoral work with Dr. Skell at The Pennsylvania State University, he recently joined the Rohm and Haas Company.

to the Goldfinger hypothesis,[3] with bromine atom as

hydrogen abstractor and the *N*-bromosuccinimide serving as a scavenger of hydrogen bromide and source of further bromine.

Massive evidence can be cited for the intermediacy of bromine atoms in NBS-containing systems.[4] The chemical properties of succinimidoyl radical went almost without recognition for nearly three decades; the nearly simultaneous observations from Traynham's[5] and our laboratories[6] were the opening wedges which led to the present understanding.

While the properties of imidoyl radicals are novel in a number of respects, the most unexpected feature which came to light was that *two imidoyl radicals were being generated in thermal chain reactions*, ground state (π) and a metastable excited state (σ_N and/or σ_O).

(1) K. Ziegler, A. Späth, E. Schaaf, W. Schumann, and E. Winkelmann, *Justus Liebigs Ann. Chem.*, **551**, 80 (1942).

(2) (a) G. F. Bloomfield, *J. Chem. Soc.*, **114** (1944); (b) D. H. Hey, *Annu. Rep. Chem. Soc.*, **41**, 184 (1944); (c) C. Djerassi, *Chem. Rev.*, **43**, 271 (1948).

(3) (a) J. Adam, P. A. Gosselain, and P. Goldfinger, *Nature (London)*, **171**, 704 (1953); (b) P. A. Gosselain, J. Adam, and P. Goldfinger, *Bull. Soc., Chim. Belg.*, **65**, 533 (1956).

(4) (a) F. L. J. Sixma and R. H. Riem, *K. Ned. Akad. Wet., Ser. B*, **61**, 183 (1958); (b) B. P. McGrath and J. M. Tedder, *Proc. Chem. Soc., London*, **80**, (1961); (c) R. E. Pearson, and J. C. Martin, *J. Am. Chem. Soc.*, **85**, 354, 3142 (1963); (d) C. Walling, A. L. Rieger, and D. D. Tanner, *ibid.*, **85**, 3129 (1963); (e) G. A. Russell, C. DeBoer, and K. M. Desmond, *ibid.*, **85**, 365, 3139 (1963); (f) J. H. Incremona and J. C. Martin, *ibid.*, **92**, 627 (1970).

(5) J. G. Traynham, and Y. S. Lee, *J. Am. Chem. Soc.*, **96**, 3590 (1974).

(6) J. C. Day, M. J. Lindstrom, and P. S. Skell, *J. Am. Chem. Soc.*, **96**, 5616 (1974).

This involvement of "electronic isomers" is reminiscent of the singlet–triplet description of carbenes. There is no reason to suppose this situation is unique for the imidoyl radicals; analogous behavior may be awaiting discovery in other systems.

Aliphatic C–H Substitution

With substrates that can react readily with bromine atoms, the presence of small amounts of bromine preempts the succinimidoyl radical as a chain carrier. Succinimidoyl radical as chain carrier is readily observed (a) with substrates that do not react readily with bromine atoms and (b) with more reactive substrates when studied under conditions where exclusion of free bromine is attained. Free bromine concentrations can be minimized by carrying out reactions in the presence of olefins, usually those which do not have reactive allylic hydrogens (ethylene, *tert*-butylethylene).

The curious "Ziegler requirement" for the use of carbon tetrachloride solvent in allylic brominations of olefins with NBS now has the obvious rationale:[6] that of maintaining a very low concentration of NBS in the liquid phase (0.005 M solubility) and thus allowing the Br_2 to be the major radical-trapping agent even though its concentration is very low (presence of olefin).[7] To observe succinimidoyl radical chemistry, a better solvent for NBS is required. For example, cyclohexene–NBS leads to 3-bromocyclohexene exclusively in CCl_4 solvent (Br atom chain reaction) but 3- and 4-bromocyclohexenes in the ratio 5:1 in CH_3CN solvent, where NBS has 0.8 M solubility. Increasing the
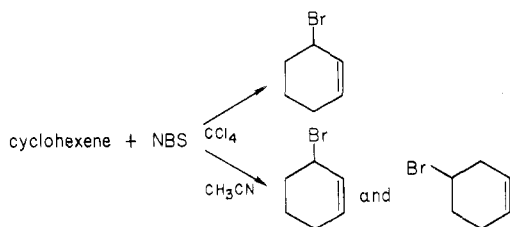
concentration of NBS changed the dominant chain carrier species from Br (in CCl_4) to succinimidoyl (in CH_3CN). Chloroform and methylene chloride are also good solvents for succinimidoyl chain reactions using NBS as the radical source.

In methylene chloride solution low-reactivity substrates such as neopentane and *tert*-butyl chloride, which cannot be brominated with Br_2 alone, can be brominated with NBS, either photoinitiated or thermally with benzoyl peroxide.[5] None of these bromi-
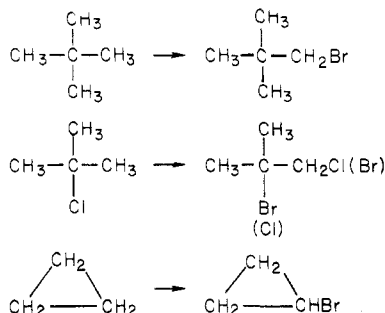
(7) It is curious that sufficient Br_2 remains in alkene solutions to be an important kinetic factor in the allylic radical bromination. Although we do not have conclusive evidence on this point, we hold the opinion that ionic addition of bromine to alkenes is not a simple bimolecular reaction, but is at least second order in Br_2, perhaps higher, and thus the rate of Br_2 disappearance falls off rapidly at low concentrations of Br_2.

Chart I[a]

$CH_3-CH_2-CH_2-CH_3 \rightarrow$		
Br_2	0	100
Br_2 with NBS	0	100
Cl_2	32	68
NCS with olefin	25	75
NBS with olefin	25	75
NIS with olefin	23	77

[a] NCS = *N*-chlorosuccinimide, NIS = *N*-iodosuccinimide.

nations take place at appreciable rates with Br_2 as the brominating agent.

More reactive substrates which can be halogenated by bromine alone make an interesting contrasting situation (see Chart I).

Bromine atom chains dominate the chemistry with the NBS–Br_2 reagent system, but if Br_2 is scavenged, NBS shows a very different reactivity. Since the reactivity is the same for NCS, NBS, and NIS, it must be attributed to a succinimidoyl radical.

Similarly contrasting results were obtained with propane, hexane, 2,3-dimethylbutane, 2-chloropropane, 3-chloropentane, and 1-bromobutane. With butane, the ratio of attack on primary and secondary hydrogens is close enough for chlorine and NCS to raise the possibility that with NCS there could be some Cl_2 chain contribution. It is clearer in the case of 2,3-di-

| $(CH_3)_2CH-CH(CH_3)_2 \rightarrow$		
Cl_2	59%	41%
NCS and C_2H_4	36%	64%
NBS and C_2H_4	39%	61%
Br_2	0%	100%

methylbutane that the Cl_2 chain reaction is effectively eliminated by the inclusion of ethylene in the reaction mixture.

The observation that the same selectivity for hydrogen abstraction is shown by NCS, NBS, and NIS leaves no alternative but to ascribe it to the succinimidoyl radical. Its reactivity is similar to that of chlorine atom, and it is reasonable to describe *the transition state as one in which C–H bond breaking is small*.
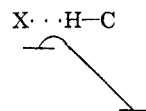
Other Haloimidoyl Reagents

A parasitic reaction which is often encountered in NBS reactions is the opening of the ring to make the isomeric β-bromopropionyl isocyanate.[4c,d,8] There are
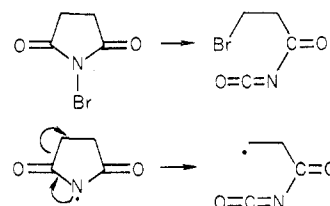

numerous additional statements on this subject, some

(8) (a) H. W. Johnson, Jr., and D. E. Bublitz, *J. Am. Chem. Soc.*, **80**, 3150 (1958); (b) J. C. Martin and P. D. Bartlett, *ibid.*, **79**, 2533 (1957); (c) J. C. Martin, private communication.

of which are contradictory and incorrect. However, Martin and co-workers[8c] have extensive evidence which implicates the succinimidoyl radical as the ring-opening species.

This ring-opening reaction can account for as much as 70% of the consumed NBS under some conditions. The same problem is encountered in using *N*-iodo-succinimide, but *N*-chlorosuccinimide shows no ring-opening reactions. This puzzling behavior will be left for later.

The ring-opening reactions can be avoided by altering the ring; compounds which do not undergo ring openings are *N*-halophthalimide, -glutarimide, -3,3-
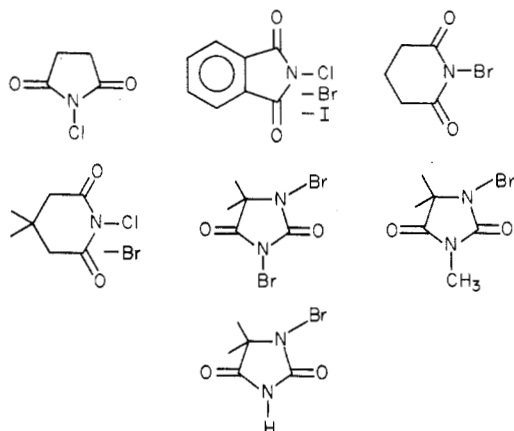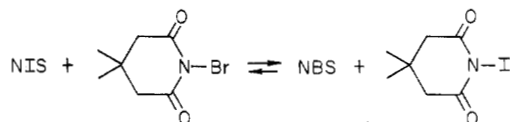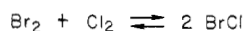

dimethylglutarimide, and a variety of *N*-bromo-hydantoins.[9] These are useful reagents.
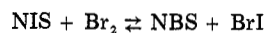
The radical-trapping ability of a number of halogenating agents can be placed in descending order for rates of transfer of a halogen atom to a radical: Br_2, *t*-BuOBr $\gg$ *N*-bromo imides, *t*-BuOCl, Cl_2 > *N*-chloro imides. A variety of qualitative observations lead to these conclusions, important among these being the observation that Br_2 is ~10^3 times more effective than NBS in trapping optically active free radicals.[10]

Competitions between these radical-trapping reagents might seem to be the best way to obtain, in quantitative form, the information given above as a qualitative inequality. However, in competitions with one another, the kinetic analysis is complicated by a number of factors:
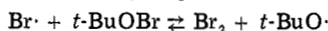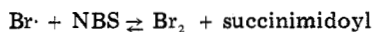
(1) radical-initiated equilibration of the reagents

$$Br_2 + Cl_2 \rightleftharpoons 2\ BrCl$$

(2) ionic equilibrium

$$NIS + Br_2 \rightleftharpoons NBS + BrI$$

(3) equilibria between radicals and reagents

$$Br\cdot + NBS \rightleftharpoons Br_2 + \text{succinimidoyl}$$

$$Br\cdot + \textit{t}\text{-BuOBr} \rightleftharpoons Br_2 + \textit{t}\text{-BuO}\cdot$$

A knowledge of rates of equilibration and equilibrium constants, most currently not known, would be required

Table I

reagent				
Br_2 (25 °C)	1	84	14	0
NBS–Br_2 (25 °C)	1	84	14	0
NBS–olefin (25 °C)	7	31	44	18
t-BuOBr (45 °C)	25	30	39	6
t-BuOBr–Br_2 (1:1, 45 °C)	23	32	39	6

Chart II

reagent		
Br_2	no reaction	
t-BuOBr (0.4 M)	47	53
t-BuOBr (~ 0.0 M)[11a]	2	98
NBS–Br_2 (0.5 M)	59	41
NBS–Br_2 (0.01 M)	9	91
t-BuOCl[11a]	10	90

for detailed interpretations in these systems. Nonetheless some instructive information can be gleaned from experiments such as the halogenations of 1-bromobutane and *tert*-butyl chloride (see Table I).

With Br_2 the products are characteristic of $Br\cdot$ attack with anchimeric assistance.[11a,12] With *t*-BuOBr[11] and NBS, *t*-BuO· or S· attack occurs without anchimeric assistance (see Chart II). The NBS–Br_2 mixed reagent shows exclusively the behavior characteristic of $Br\cdot$, although NBS is the only reagent undergoing net consumption; *t*-BuOBr–Br_2 reagent shows the behavior characteristic of *t*-BuO· radical. However, if the substrate is a less reactive one, the mechanism of halogenation is different. For example, when *t*-BuCl is the substrate, the NBS–Br_2 system shows the reactivity of succinimidoyl radical rather than $Br\cdot$. The NBS–Br_2 experiments *require* a three-step chain sequence: hydrogen atom abstraction from this unreactive substrate by succinimidoyl radical, trapping by Br_2 of the ·C_4H_8Cl, and regeneration of the succinimidoyl radical by the halogen exchange process.

The extent of rearrangement of the primary radical intermediate is determined by the concentration and reactivity of the trapping agents.[11a]

Additions to Double Bonds[13]

There are widely scattered comments in the literature about additions of halo amides and halo imides to double bonds, but often the product structures were not

(9) For the use of bromohydantoins in a variety of brominations, see: O. I. Orazi, R. A. Corral, and J. D. Bonafede, *Anal. Asoc. Quim. Arg.*, **45**, 139, 151 (1957); H. J. Schumacher, O. O. Orazi, and R. A. Corral, *ibid.*, **40**, 19 (1952).

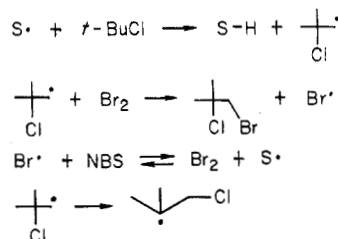(10) P. S. Skell, D. L. Tuleen, and P. D. Readio, *J. Am. Chem. Soc.*, **85**, 2850 (1963).

(11) (a) P. S. Skell in "Organic Reaction Mechanisms", The Chemical Society, Special Publication No. 19, Burlington House, London, 1965, p 131; (b) K. Ody, A. Nechvatal, and J. M. Tedder, *J. Chem. Soc., Perkin Trans. 2*, 521 (1976).

(12) P. S. Skell and K. J. Shea, "Free Radicals", J. Kochi, Ed. Wiley, New York, N.Y., 1973.

examined and the importance of ionic additions, while recognized, was not evaluated.

Double bond addition products can be obtained by photoinitiation of reactions (no dark reactions) between the *N*-halo imide and olefins in CH_2Cl_2 solvent. Some of the compounds isolated are listed below. Additions
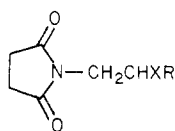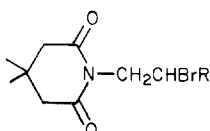
X = Br, Cl; R = H, *t*-Bu   R = *t*-Bu, C_6H_5

to unsymmetrical olefins show that the imidoyl radical became attached to the least substituted atom of the double bond. With NBS (but not NCS), substantial amounts of the reagent are converted to β-bromo-propionyl isocyanate. The amount of loss to rearranged product is *less* at higher olefin concentrations.

Competition: Abstraction vs. Addition[13]

The competition consumption of succinimidoyl in ethylene–neopentane mixtures (CH_2Cl_2 solvent) leading to 1,2 adducts and neopentyl halides, respectively, was found to be independent of the source of the succin-imidoyl radical. On a per molecule basis, the relative rate ratio k_{abstr}/k_{addn} is 0.22. Varying the mole ratio of ethylene and neopentane reactants did not change this value. The quotient k_{abstr}/k_{addn} for neopentane vs. *tert*-butylethylene is 0.15. Since the abstraction rate is the same, *tert*-butylethylene adds succinimidoyl 1.5 times as fast as ethylene. A correction for statistical difference may not be necessary if addition to the double bond by the imidoyl radical is from the π direction in both cases.

The comparison for Cl· can be obtained from the –9 °C radical-chain chlorination of 1-butene,[14] comparing abstraction at the terminal methyl group with addition: k_{abstr}/k_{addn} = 0.052. For comparison, the succinimidoyl values from the neopentane–*tert*-butylethylene experiments must be divided by 4 to put
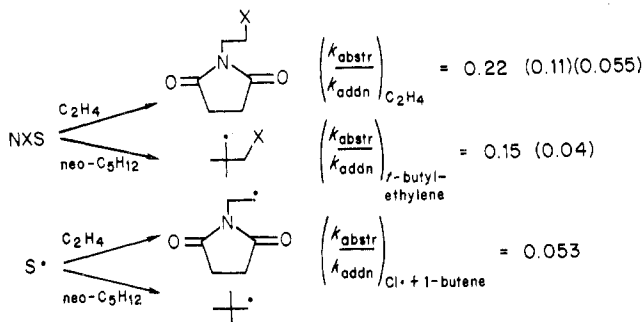
it on a per methyl group basis: k_{abstr}/k_{addn} = 0.04. *The similarity of Cl· and succinimidoyl is emphasized.*

Imidation of Arenes[13]

While it is often stated and generally believed that arenes are inert to reaction in NBS-radical systems, this is not the case. Arenes react readily. For example, benzene with *tert*-butylethylene (as Br_2 scavenger) reacts with NBS (benzoyl peroxide initiation) to produce *N*-phenylsuccinimide, succinimide, and ethylene

(13) J. C. Day, M. G. Katsaros, W. D. Kocher, A. E. Scott, and P. S. Skell, *J. Am. Chem. Soc.*, 100, 1950 (1978).
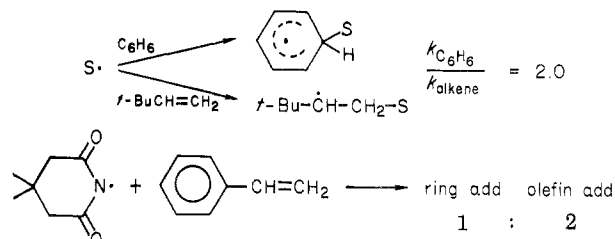(14) M. L. Poutsma, *J. Am. Chem. Soc.*, 87, 2172 (1965).

Scheme I
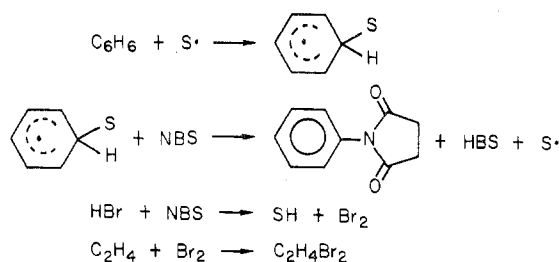
dibromide in 1:1:1 ratio. There is no parasitic loss of NBS to β-bromopropionyl isocyanate in this system. A reasonable chain reaction sequence is given in Scheme I.

This is a new reaction which introduces a nitrogen substituent into the arene nucleus. Unfortunately the reaction shows no great selectivity between the various ring positions of chlorobenzene or naphthalene, but nonetheless may have synthetic utility in some instances.

Alternate reactions dominate if the arene is readily brominated, either in the ring, such as anthracene to yield 9-bromoanthracene, or in benzylic positions to produce benzyl halides; these are Br· chain substitution processes which are not eliminated by the inclusion of olefins in the reaction mixture.

Competition: Arene vs Alkene[13]

It is remarkable that benzene and olefins have similar affinities for addition of succinimidoyl radical. The relative rates of addition are obtained by determining the yields of *N*-phenylsuccinimide and the 1,2 adduct of NBS to *tert*-butylethylene; benzene adds succin-

imidoyl twice as fast as *tert*-butylethylene. If a statistical factor is applied, each position of benzene is one-third as reactive as the terminal position of *tert*-butylethylene. In line with these results is the observation that 3,3-dimethylglutarimidoyl attack on styrene occurs only twice as frequently on the double bond as on the phenyl nucleus. This radical shows a remarkable insensitivity to the energetics of product formation. Therefore, *the transition state is remarkably unlike the product.*

In alkene vs. arene addition competitions, imidoyl radicals behave much like the hydroxyl radical.[15] More commonly, radical additions to olefins are greatly favored over arene addition. For example, $k_{arene\ addn}/k_{olefin\ addn} \approx$ 0.01–0.02 for CH_3· and CF_3·.[16] Other

(15) L. M. Dorfman and G. E. Adams, National Bureau of Standards Report No. NSRDS-NBS-46, U. S. Government Printing Office, Washington, D.C., 1973.
(16) M. Swarc, and J. M. Binks, "Theoretical Organic Chemistry, Kekule Symposium", Butterworths, London, 1959, p 262; "Evaluated Kinetic Data on Gas Phase Addition Reactions: Reactions of Atoms and Radicals with Alkenes, Alkynes, and Aromatic Compounds", J. A. Kerr and M. J. Parsonage, Ed., Butterworths, London, 1972.

Table II[a]

$$\text{neo-}C_5H_{12} \xrightarrow{} XH + \text{neo-}C_5H_{11}\cdot$$
$$X\cdot$$
$$CH_2Cl_2 \xrightarrow{} XH + \cdot CHCl_2$$
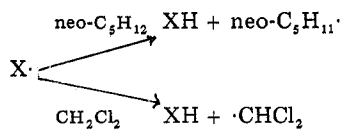
reagent	$(k_{\text{neo-}C_5H_{12}}/k_{CH_2Cl_2})_{\text{per H}}$
NBS-olefin	23
NBS-Br$_2$	1.0
NIS-I$_2$	1.0
NBP-olefin	12.5
NBP-Br$_2$	0.5
NIP-I$_2$	0.5
NBDMG-olefin	4.0
NBDMG-Br$_2$	1.0
Br$_2$[b]	0.1

[a] NXS, *N*-halosuccinimides; NXP, *N*-halophthalimides; NBDMG, *N*-bromo-3,3-dimethylglutarimide. [b] Bromination is slow, 3% consumption of bromine after 4-h irradiation.

species, such as the alkoxy radicals, show little tendency to add to arenes, and in its reactions with alkenes hydrogen abstraction by alkoxy radical is favored over addition to the double bond.[17]

For hydroxyl radicals, at 25 °C, $k_{\text{benzene}}/k_{\text{ethylene}} = 4.3$.[15] Absolute rate constants are 10^8–10^9 L/(mol s) for these additions, close to values for encounter-controlled processes.[15] Absolute rate constants for imidoyl radical additions to arenes are likely to be close to these values.

Two Thermally Accessible States for Succinimidoyl[18]

The kinetic experiments to be described require two succinimidoyl radical intermediates. Unfortunately failure has attended all attempts to obtain spectroscopic corroboration; no ESR transient has been observed,[19] and no UV-absorbing transient has been identified in flash photolyses.[20]

Imidoyl radicals as the chain-carrying hydrogen-abstracting intermediates can be attained under a variety of conditions with relatively unreactive substrates such as neopentane, *tert*-butyl chloride, and methylene chloride. The competitive halogenation results for two of these substrates are given in Table II.
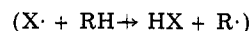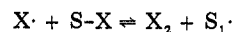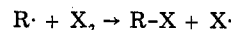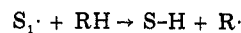
Exchanges between product radicals and starting materials were demonstrated not to take place under these conditions by examining the recovered starting materials in an experiment using CD$_2$Cl$_2$ as solvent.

$$\text{—}\overset{\cdot}{+} + CH_2Cl_2 \rightleftharpoons \text{—}\overset{\cdot}{+}\!+ \cdot CHCl_2$$
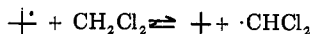
Identical selectivities are obtained with (bromo imides + Br$_2$) or (iodo imides + I$_2$) reagents, leaving no alternative but to ascribe the hydrogen-abstracting steps to imidoyl radicals; the imides are the only nitrogen-containing products. Under these conditions an imidoyl radical, (S$_1$·), is invoked. This imidoyl radical shows approximately equal reactivity toward the C–H bonds

of CH$_2$Cl$_2$ and neopentane. Also, in the case of succinimidoyl, in the presence of Br$_2$ *there is no opening of the ring* to give the product BrCH$_2$CH$_2$C(O)N= C=O.

Since Br$_2$ and I$_2$ are much better radical trapping agents than the halo imides, three-step chain processes are required:

$$S_1\cdot + RH \rightarrow S\text{-}H + R\cdot$$
$$R\cdot + X_2 \rightarrow R\text{-}X + X\cdot$$
$$X\cdot + S\text{-}X \rightleftharpoons X_2 + S_1\cdot$$
$$(X\cdot + RH \rightarrow HX + R\cdot)$$

The third step, in which S$_1$· is regenerated, is a near thermoneutral step.[21]

The reactions carried out in the presence of small amounts of bromine-scavenging olefins show a strikingly different selectivity. Neopentane, despite its stronger C–H bonds, is considerably more reactive than CH$_2$Cl$_2$. The only nitrogen-containing product (apart from a minor amount of olefin addition product) is imide for each of the *N*-halo imides, except for the *N*-halosuccinimides. A rearrangement product, β-halopropionyl isocyanate, can be a major product (40–70%) when NBS or NIS is used.

This altered selectivity is impossible to explain with a single hydrogen-abstracting imidoyl radical. While olefin might consume imidoyl radical in an addition process, or X$_2$ cause return of imidoyl radical to halo imide, the presence of olefin or halogen cannot affect the competition between neopentane and methylene chloride.
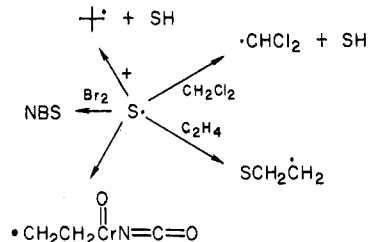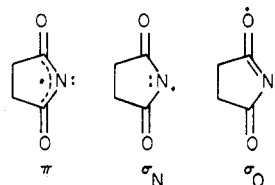

These observations can be explained if a second imidoyl radical is postulated as an intermediate. This second imidoyl radical, S$_2$·, is generated in the exo-

$$R\cdot + S\text{-}X \rightarrow RX + S_2\cdot$$
$$S_2\cdot + RH \rightarrow S\text{-}H + R\cdot$$
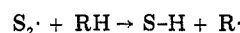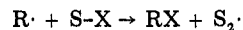
thermic reaction (~ 20 kcal/mol) of an alkyl radical with S–X in the chain-propagation sequence. This radical is far less sensitive to the bond strength of its prey, and it *undergoes the ring-opening reaction* in the succinimidoyl system.

Three structures for succinimidoyl radical can be reasonably represented by VB formulations:

$$\pi \qquad \sigma_N \qquad \sigma_O$$

(17) C. Walling and R. T. Clark, *J. Am. Chem. Soc.*, **96**, 4530 (1974).
(18) P. S. Skell and J. C. Day, *J. Am. Chem. Soc.*, **100**, 1951 (1978).
(19) (a) A. G. Davies, B. P. Roberts, and J. M. Smith, *J. Chem. Soc., Perkin Trans. 2*, 2221 (1972); (b) G. R. Chalfont, and M. J. Perkins, *J. Chem. Soc. B*, 401 (1970); (c) E. Hedaya, R. L. Hinman, V. Schomaker, S. Theodoropulos, and L. M. Kyle, *J. Am. Chem. Soc.*, **89**, 4875 (1967).
(20) P. S. Skell, unpublished results.

(21) P. B. Howard and H. A. Skinner, *J. Chem. Soc. A*, 1536 (1966). Unfortunately there is no good value known for the N–X bond energy in the halo imides, only an estimate which indicates the value is approximately that of the corresponding X$_2$ molecule.[18]

It is incorrect to consider these three representations as canonical contributors to a hybrid structure since they have orthogonal orbital systems; these are best considered as electron isomers (analogous to triplet and singlet carbenes), or ground state and two excited states for which there might be some forbiddenness for light-emission relaxations. At any rate, thermal reaction processes are faster than relaxation.

Koenig et al. have done INDO calculations, including the effect of deformation of structure, and have concluded that π is ground state, σ_N and σ_O are excited states.[22]

A satisfactory mechanism must address itself to the following circumstances: (1) NBS traps alkyl radicals approximately 1000 times less rapidly than Br_2; (2) there are two varieties of succinimidoyl radical, one $(S_2\cdot)$ which shows a stronger preference for the hydrogen from an alkane than from methylene chloride, the other $(S_1\cdot)$ having equal reactivity toward these two substrates; (3) in the case of succinimidoyl radicals, $S_2\cdot$ undergoes ring opening, $S_1\cdot$ does not. A construct which accommodates these conditions identifies $S_2\cdot$ with the σ_N and $S_1\cdot$ with the π formulations.

Since $S_2\cdot$ is the excited state, it abstracts an H atom from a substrate in a reaction more exothermic than $S_1\cdot$, the difference in heat of reactions being approximately
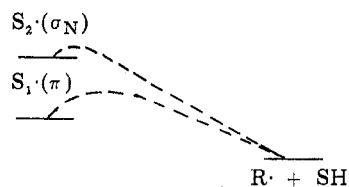

the difference in energy of the radicals. It is reasonable to assign less C–H bond breaking to the $S_2\cdot$ transition state than to the $S_1\cdot$. Thus, $S_2\cdot$, like Cl·, is insensitive to factors which stabilize the product radical, R·, but is sensitive to some polar characteristic of the substrate. Although the C–H bond energy of neopentane is 6–8 kcal/mol larger than the C–H bond energy of CH_2Cl_2, $S_2\cdot$ and Cl· react preferentially with neopentane. The more stable succinimidoyl, $S_1\cdot$, makes a transition state with more C–H bond stretching, and thus is more sensitive to the bond strengths of the substrate.

Within this framework, the 1,2-addition reactions of halo imides to olefins should be described as $S_2\cdot$ chemistry. Possibly the same is true for additions to arenes since the high reactivity of arenes relative to alkenes is characteristic of a highly exothermic process, wholly insensitive to the energetics of product formation.

The step leading to $S_1\cdot$, abstraction of halogen from NXS by a halogen atom, is most likely a nearly thermoneutral step since best estimates place the energy of the N–X bonds near those of the corresponding halogens.[21] Clearly the formation of $S_2\cdot$ from NXS + X· would be too endothermic to occur to any appreciable extent. The reaction of NXS with R· is sufficiently exothermic to make $S_1\cdot$ or $S_2\cdot$, but chooses to make $S_2\cdot$ only. The failure of R· + NXS to follow the more exothermic path to $S_1\cdot$ is perhaps an example of
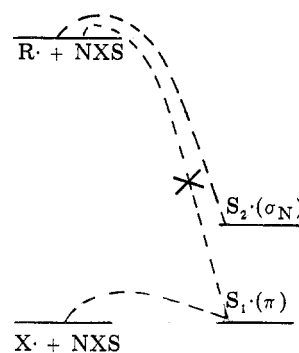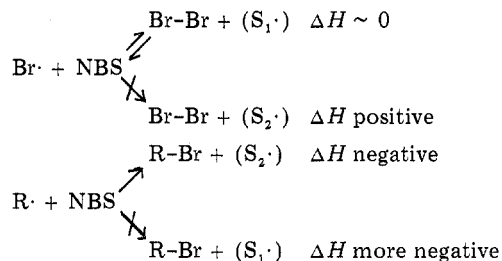
some principle of least change, similar to a Franck–Condon effect, or the spin-conservation rules. As the N–Br bond is stretched, the molecular orbital which is being pulled apart most closely resembles an sp^2 atomic
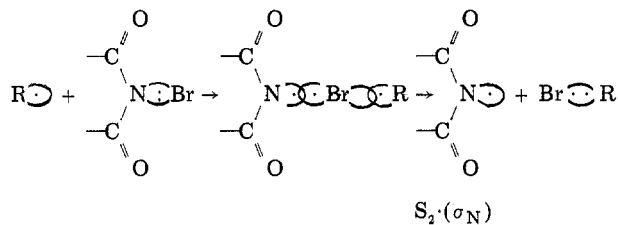
orbital on nitrogen; the odd electron remains in this orbital without requiring a reorganization of the imide π system.

It is intriguing to speculate that the reaction of X· with an N-halo imide leads to $S_1\cdot(\pi)$ through a mechanism involving the initial attachment of X· above the plane of the ring, thus perturbing the π system prior to the departure of X_2.

The reaction of R· with Br_2 is exothermic by approximately 20 kcal/mol. If the reaction of R· with NBS went to R–Br + $S_1\cdot$, the exothermicity would be the same and it would be reasonable to anticipate a rate approximately one-half the Br_2 rate (statistical factor) for trapping alkyl radicals. The favoring of the path to $(S_2\cdot)$, a less exothermic pathway, implicates a higher activation energy process and thus accounts for the N-halo imides having lower reactivities than the halogens in trapping alkyl radicals.

Finally, Koenig et al.[22] recognized a symmetry correlation between σ_N and the ring-opened radical, but not with π, another concordance.

Ring-Opening Reactions of $(S_2\bullet)$ Succinimidoyl Radicals[23]

A puzzle which has been apparent for some 20 years is now rationalized. Among the imidoyl systems NBS and NIS (but not NCS or halophthalimides, or -glutarimides) are converted to $XCH_2CH_2C(O)NCO$, under
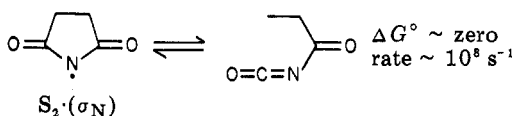
(22) T. Koenig and A. Wielesek, *Tetrahedron Lett.*, 2007 (1975).

(23) P. S. Skell, J. C. Day, and J. P. Slanga, *Angew. Chem.*, **90**, in press.

$S_2\cdot$ conditions, even though the same $S_2\cdot$ radical is generated in NCS reactions.

The requirement that some olefin be present for this rearrangement to occur is explained. In the absence of olefin such systems develop some Br_2 which interferes in one of two different ways. With reactive substrates, Br· carries the chain so there are no succinimidoyl radical intermediates. With substrates which do not react with Br·, the $S_1\cdot$ is the hydrogen-abstracting chain carrier, and it does not correlate with the ring-opened intermediate.

The failure to obtain $ClCH_2CH_2C(O)NCO$ from NCS under $S_2\cdot$ reaction conditions is explained by a rapid reversible ring-opening process. The open-chain radical is trapped by NBS and NIS, but NCS reacts too slowly

$$O=\overset{\displaystyle\diagup\!\!\!\diagdown}{\underset{\underset{\displaystyle S_2\cdot(\sigma_N)}{N}}{}}=O \;\rightleftharpoons\; \underset{O=C=N}{\diagup\!\!\!\diagdown}=O \quad \begin{array}{l}\Delta G^\circ \sim \text{zero}\\ \text{rate} \sim 10^8 \ s^{-1}\end{array}$$

to interfere with the hydrogen abstraction from substrate by $S_2\cdot$. This explanation is supported by the dependence of ring-opened product on NBS concentration: the lower the concentration, the less ring-opened product.

This explanation is also supported by three further lines of evidence. Succinimidoyl radicals with one or more alkyl substituents on the ring undergo ring opening exclusively under $S_2\cdot$ conditions and no hydrogen abstraction occurs. Conversely, normal hydrogen abstractions and no ring opening occur under $S_1\cdot$ conditions. In these cases the ring-opened species is a secondary or tertiary alkyl radical, and the energetics for return to $S_2\cdot$ are no longer favorable. Secondly, the succinimide recovered from *cis*-2,3-dideuterio-NCS reactions is a mixture of *cis*- and *trans*-dideuteriosuccinimide. Stereochemical equilibration implicates an open-chain intermediate even though there is no open-chain product. Finally, in the presence of large amounts of olefin the ring-opening reaction is minimized. Trapping of the $S_2\cdot$ leads to 1,2 adducts, and in the presence of arenes there is no

Chart III[a]
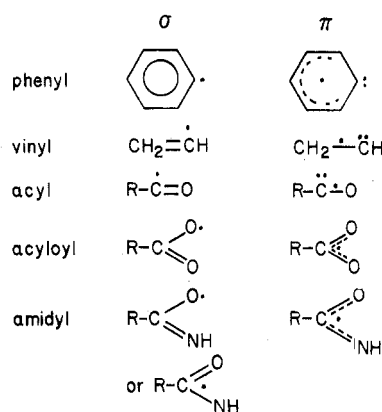
[a] These are *not* canonical contributors to a hybrid structure.

ring-opened product since trapping is too effective.

Conclusion

While the above postulate of formation of electronically excited product from thermal reactions is uncommon, it is not unknown; all chemiluminescent reactions involve formation of an excited-state product from a thermal process. Chemistries are well-known for singlet- and triplet-state carbenes. Analogous chemistries of doublet species in solution appear to have escaped prior consideration, but in studies of gas-phase processes, excited-state species have achieved some recognition; for example, the chemistries of iodine atoms in $P_{3/2}$ and $P_{1/2}$ states.

It is possible that chemistries of ground and excited doublet states have been involved, but not recognized, in well-known systems. A reexamination of radical reactions in which the intermediates are generated with different energetics may reveal these situations. Although this phenomenon is not restricted to π systems, the π systems are more easily illustrated with VB pictures. A number of them are listed in Chart III.

Correlation of Molecular Orbital and Valence Bond States in π Systems

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We define the "truth" in the π electronic theory of organic chemistry as a complete configuration-interaction (CI) calculation with a semiempirical Hamil-

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tonian of the Hubbard or the Pariser–Parr–Pople type. Molecular orbital (MO) theory, in zero order, presents an imperfect view of this "truth" because it fails to predict the "true" order, the degeneracies, and/or the absolute energies of the MO states. We note that the electrons in a zero-order MO state are *delocalized* because the MOs extend over the entire molecule and are *uncorrelated* because the MOs are computed from