Tetrahedron Vol. 41, No. 19, pp. 4289 to 4302, 1985
Printed in Great Britain.

0040-4020/85 $3.00 + .00
Pergamon Press Ltd.

IMIDYL RADICALS

Ulrich Lüning

and

Philip S. Skell*

Department of Chemistry
The Pennsylvania State University
152 Davey Laboratory
University Park, Pennsylvania 16802

(*Received in Germany* 18 *April* 1985)

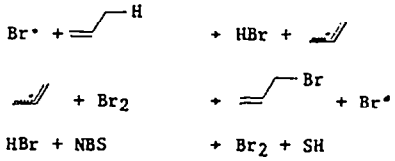
Abstract - Under reaction conditions which prevent halogen atom chains, imidyl radicals are the chain carriers in reactions of N-haloimides. Characteristic reactions are 1) ring-opening of certain imidyl radicals, 2) hydrogen abstractions with selectivities similar to chlorine atoms, 3) additions to alkenes and 4) substitutions of arenes. The absolute rate constant of reaction between imidyl radicals and most substrates is in a range of $>10^5$ ℓ/mol. sec.

HISTORICAL

Despite determined earlier efforts to recognize the intermediacy of succinimidyl radicals, only during the last decade was this objective achieved.

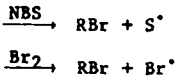
Radical reactions using N-haloimides have been known since 1942, when Ziegler et al.[1] reported radical allylic brominations using N-bromosuccinimide (NBS) in $CC\ell_4$. A critical factor for success in these allylic brominations was the use of $CC\ell_4$ as the medium, a system in which NBS is slightly soluble ($\sim 10^{-3}$ M).

This reaction first was explained, without evidence, as a radical chain reaction with a succinimidyl radical as the hydrogen abstractor.[2] In 1953 Goldfinger and coworkers proposed a bromine atom based mechanism,[3] in which NBS only served as an HBr scavenger thus forming succinimide (SH) and bromine. Although the presence of alkene dictates a very low Br_2



concentration, the small amounts of bromine which are present[4] are sufficient to maintain a Br• chain. Allylic bromination occurs in the absence of NBS when Br_2 is added slowly (in a He stream) to an alkene.[5a,b]

The low solubility of NBS in $CC\ell_4$ is the crucial factor in precluding imidyl reactions under Ziegler conditions.[6] In contrast, if a solvent is used in which NBS has a higher solubility (i.e. acetonitrile, methylene chloride), NBS can compete successfully with the small amounts of Br_2, in



reactions with the alkyl radical intermediates. In good NBS solvents, succinimidyl radicals are formed, and if the scavenging of Br_2 is adequate, the chemistry is attributable totally to the imidyl radicals. These chain carriers are unambiguously recognized by the presence of imidyl moieties in products obtained in addition reactions. Indications for their participation in substitution reactions come from the distinctive substitution selectivities.[6,7,8]

Small amounts of alkenes without allylic hydrogens serve adequately to scavenge bromine in these "better" NBS solvents. The influence of small amounts of alkene on the selectivity of the halogenation of butane is shown in Table 1.[8]

Table 1

Distribution of isomers (%) formed in halogenations of butane with various halogenation reagents.[8]

	1-halobutane	2-halobutane
Br_2	0	100
Br_2/NBS	0	100
Cl_2	32	68
NCS/alkene	25	75
NBS/alkene	25	75
NIS/alkene	23	77

While bromination of butane with NBS in the presence of Br_2 shows $Br^{\bullet}$ selectivites, the inclusion of alkenes changes the selectivity to one resembling $Cl^{\bullet}$. The same selectivity is found for different N-haloimides [N-chlorosuccinimide (NCS), N-bromosuccinimide (NBS) and N-iodosuccinimide (NIS)], thus proving that a succinimidyl radical is the hydrogen abstracting intermediate. Prior to this discovery, the only hints for succinimidyl radicals were the isomerization of NBS to β-bromopropionyl isocyanate (BPI),[9] some radical-scavenging, and ESR experiments.[10]

Using the alkene-scavenging conditions, the chemistry of a number of imidyl radicals have become accessible. The key to imidyl radical chemistry is: 1) avoid competing halogen chains by scavenging halogen (and halogen atoms) with alkenes, and 2) use solvents in which the N-haloimides are soluble.

IMIDYL RADICAL CHAINS

An imidyl radical chain mechanism was confirmed by chain length measurements.[11,12] Quantum yield determinations of photochemically induced brominations of methylene chloride by NBS in the presence of t-butylethylene (in the dark no reaction takes place) showed chain lengths for alkane brominations of approximately 30, with inhibition by oxygen or 2,6-di-tert.-butyl-p-cresol.[11] Chain lengths of $\sim 10^3$ are attained for additions to alkenes,[14] and 10 for substitutions on benzene.[15] The chain reactions can also be induced by thermal decomposition of initiators such as di-tert.-butyl peroxyoxalate, benzoyl peroxide or AIBN.[11,12]

Besides the confirmation of the chain character of this reaction, it was shown, that the chain propagating radical is an imidyl radical since it undergoes addition reactions with alkenes and arenes and thus becomes part of the product molecules (see below).[8,13,14,15]

Some Chain Sequences

Substitutions: $S^{\bullet} + RH \rightarrow SH + R^{\bullet}$

$R^{\bullet} + NBS \rightarrow RBr + S^{\bullet}$

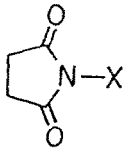
Additions: $S^{\bullet} + = \rightarrow S\!-\!\overset{\bullet}{\!/}$

$S\!-\!\overset{\bullet}{\!/} + NBS \rightarrow S\!\sim\!Br + S^{\bullet}$

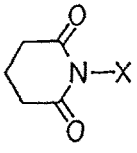
SCOPE OF IMIDYL RADICALS AND THEIR REACTIONS

The halogen scavenging recipe is useful in generating imidyl radicals from a variety of N-haloimides. Both the halogen and the imidyl part can be varied:

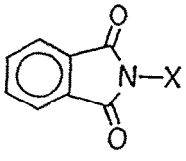
N-halosuccinimides:



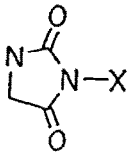
N-haloglutarimides:



N-halophthalimides:



N-halohydantoins:



These imidyl radicals can participate in: 1) ring-opening reactions, 2) hydrogen abstractions, 3) alkene additions and 4) reactions with arenes.

1. Ring-Opening Reactions

An important reaction of imidyl radicals is the ring-opening reaction forming isocyanates, a reaction known since 1957;[9] this is a chain reaction.[11] In the proposed mechanism the imidyl radical opens to form a carbon centered radical with an acylisocyanate function. This radical abstracts a halogen from the N-haloimide to form the halo-acylisocyanate with regeneration of the chain propagating imidyl radical. Table 2 shows which N-haloimides ring open and which do not.[11]

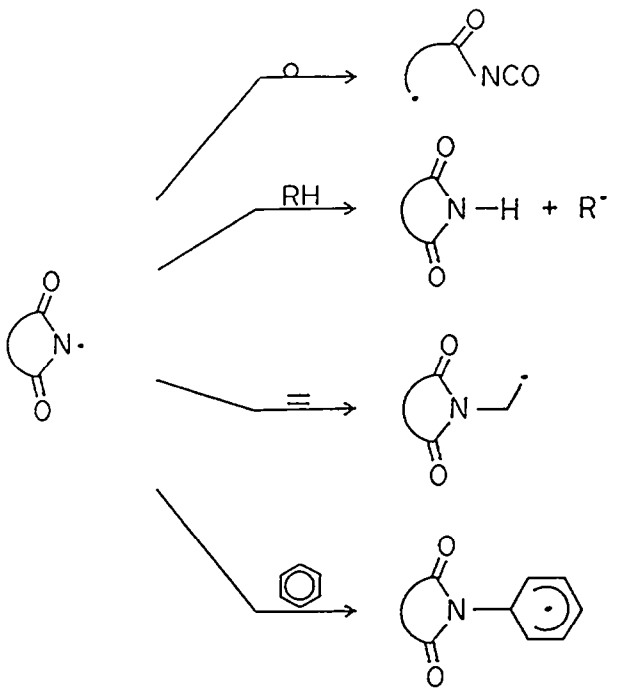
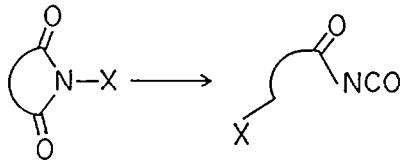


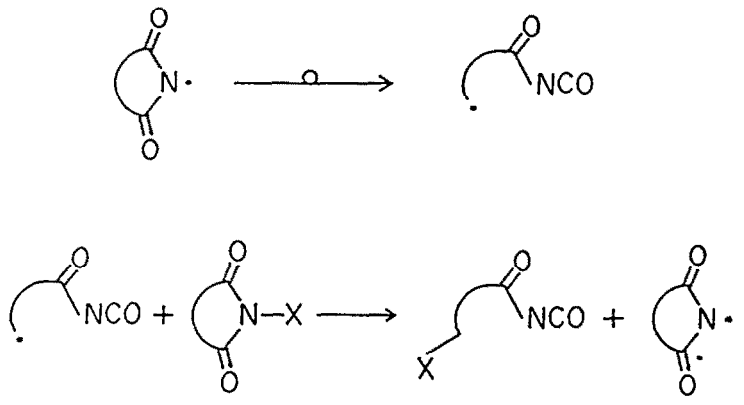
Table 2[ab]



Form Isocyanates	Do Not
NBS	NCS
NIS	23DMNCS
23DMNBS	NCG
22DMNCS	NBG
22DMNBS	33DMNCG
2MNBG	33DMNBG
22DMNBG	NCP
	NBP
	NIP
	N-bromohydantoins

a) S stands for succinimide, G for glutarimide, P for phthalimide, C for chloro, B for bromo, I for iodo, M for methyl and DM for dimethyl. So, i.e., 23DMNCS is an abbreviation for N-chloro-2,3-dimethyl succinimide.

b) ref. 11

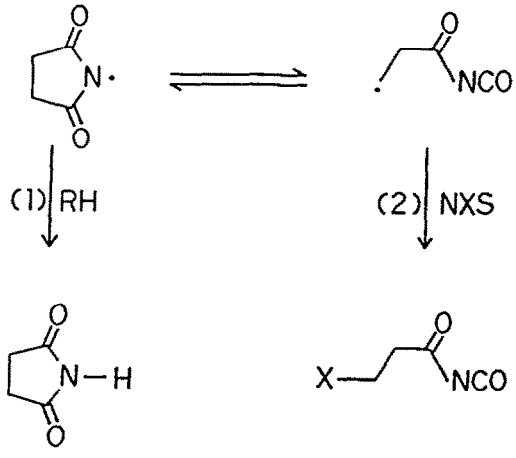


In some halogen scavenged systems this ring-opening reaction occurs with 96% yield.[11] The ring-opening is in competition with abstraction and addition reactions with suitable substrates such as neopentane,[11] t-butylethylene,[11] or benzene,[15] the presence of which reduce the extent of ring-opening.

However, there were several puzzling observations: 1) the yield of ring-opened product is dependent on the N-haloimide concentration,[11] 2) NBS forms ring-opening products, NCS does not,[11] and 3) the yields of isocyanates are larger if α-alkyl substituents are present on the N-haloimides.[11] These facts suggested reversibility of the ring-opening reaction.

Ultimately the reversibility of the ring-opening was proved by using the deuterium labeled N-halosuccinimides, meso-and d,ℓ-2,3-dideutero-N-halosuccinimides (meso-d_2-NXS, d,ℓ-d_2-NXS).[11] Using the deuterium labeled N-chlorosuccinimides meso-d_2-NCS or d,ℓ-d_2-NCS in chlorinations of neopentane (ethene halogen scavenger) the succinimide obtained was found to be 90% isomerized indicating a ring-opening/ring-closure intervention, even though there is no ring-opened product with NCS. If meso-d_2-NBS was used to brominate neopentane, 84% of the NBS was converted to β-bromopropionylisocyanate (BPI), the remaining 16% effecting substitution on neopentane; 62% of the succinimide formed in this substitution reaction had undergone ring-opening. This difference is explained with a more rapid trapping of the ring-opened radical by NBS than by NCS. The results are summarized in Scheme I.

Scheme I



NCS: rate (1) > rate (2), and thus no isocyanate is obtained and deuterium scrambling in the succinimide is observed.

NBS: rate (2) > rate (1) and thus ring-opened product dominates and less deuterium scrambling is found in the succinimide.

The halogen transfer from the N-haloimide to the ring-opened radical is slower for N-chloroimides than for N-bromo-or N-iodoimides [rate (2) (NCS) << rate (2) (NBS)]. The slower trapping of the ring-opened radical results in substitution exclusively, accompanied by isotopic scrambling in the succinimide.

Methyl substituents in the α-position increase the rate of ring-opening (22DMNBG ring opens, 33DMNBG does not) and decreases the rate of ring closure by stabilizing the ring-opened radical (3° radical instead of a 1° radical).[11] Thus even a chlorocompound such as 22DMNCS produces isocyanate.[11] In benzene at 70°C 22DMNBS forms 72% isocyanate, but NBS only 1%, the remainder being involved in the substitution reaction on benzene.[15]

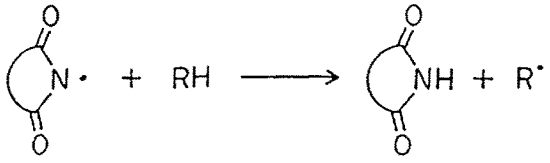
The glutarimides undergo ring-opening less rapidly than the succinimides, a consequence of difference in ring strain, and ring-opening has not been observed with phthalimides.

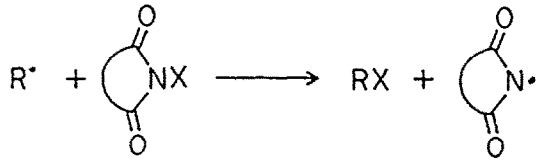
To summarize, ring-opening product is diminished by choosing N-chloroimides instead of N-bromoimides, increased by substituting the α-positions with methyl groups, and decreased by using N-haloglutar-and N-halophthalimides instead of N-halosuccinimides.

As already mentioned, the yield of ring-opening product is also influenced by other competing reactions such as H-abstractions or additions to alkenes or arenes.[11,15] For example, NBS in benzene at 70°C forms only 1% BPI (99% reacts to form N-phenylsuccinimide and succinimide).[15] Also, inclusion of such compounds as bromotrichloromethane may diminish the ring-opening yield because they favor reactions other than the imidyl chains.[16,17] Inclusion of Br_2 lowers the yield of BPI,[12,17,18] too, but to date the rationale is not fully understood. The competition between bromine atom chains and succinimidyl chains does not adequately explain the reduction in BPI yields.[12,17,18] Explanations which have been suggested include the formation of a Br•-NBS-complex,[12,19] or another state of S• (see below).

2. Hydrogen Abstractions

Hydrogen abstractions by imidyl radicals have been examined for a number of substrates. The problem of distinguishing between competitive bromine atom chains can be overcome by using substrates relatively unreactive to bromine atoms such as, for example, neopentane, methylene chloride, t-butyl chloride or 2,2-dichloropropane. More generally halogen atom chains can be avoided by scavenging of halogen and halogen atoms with alkenes as ethene, t-butylethene, or 1,1-dichloroethene for chlorine or bromine, and allene for iodine; butadiene or norbornene are necessary to preclude Br• abstractions in benzylic systems.





Benzylic hydrogen atoms react very rapidly with Br•, and in the ethylbenzene/ toluene competition a benzylic hydrogen of ethylbenzene is attacked 20-30 times faster than one of toluene. This selectivity value is obtained with Br_2, Br_2/NBS, NBS alone, or NBS/t-butylethylene.[5] However, using norbornene or butadiene as a Br• trap in this competition, 33DMNBG shows a bromination

Table 3

Hydrogen abstraction selectivities for different radicals on a per hydrogen basis.[a)]

		Cl•[b)]	S•[c)]	G•[d)]	P•[e)]	Br•[f)]
$CHCl_3$			0.0014			8.5
CH_2Cl_2		<0.02	0.06[j)]	0.18	0.14	>15
$(CH_3)_2CCl_2$[i)]			0.14			
$(CH_3)_3CCl$[i)]			0.43			
1° RH		≡1	≡1	≡1	≡1	≡1
2° RH		3.6	4.6[h)]	6-7	11	~700
3° RH		4.2	14	18	~50	>25000
	$BrXC_4H_8$					
1-bromo-butane	1,1-	0.09[g)]	0.20[c)]			0.09[f)]
	1,2-	0.43	0.54			8.1
	1,3-	≡1	≡1			≡1
	1,4-	0.46	0.43			0
k_H/k_D	CH_2Cl_2		1.5[c)]			11.5[c)]
	$CHCl_3$		1.4[c)]			13[c)]

a) S•, G• and P• stand for succinimidyl, glutarimidyl and phthalimidyl radicals.
b) 25°C, ref. 16, 21. c) 15°C, ref. 16. d) 15°C, ref. 20. e) 15°C, ref. 23.
f) 27°C, ref. 16,22. g) 60°C, ref. 25. h) ref. 17. i) Rearrangements by migration of chlorine are observed, ref. 16. j) ref. 11.

Table 4

Activation parameters for glutarimidyl (G•) and phthalimidyl radicals (P•) in neopentane/methylene chloride competitions.

	$\Delta H^{\ddagger}_{C_5H_{12}} - \Delta H^{\ddagger}_{CH_2Cl_2}$ [kJ/mol]	$\Delta S^{\ddagger}_{C_5H_{12}} - \Delta S^{\ddagger}_{CH_2Cl_2}$ [J/mol K]
G•[a)]	-10	-21
P•[b)]	-16	-37

a) ref. 20. b) ref. 23

selectivity of only 3,[20] with substitution also occuring on the ethyl group of ethylbenzene, $r(CH_2/CH_3) = 3$,[20] selectivities similar to those reported for Cℓ•. Although the main reaction in this latter system is addition to the alkene, the selectivity for benzylic substitutions are distinctly different from that of Br•.

In Table 3 selectivities on a per hydrogen basis for several imidyl radicals and various competition systems are summarized. The selectivities are similar to those of Cℓ• or OH• and differ sharply from those of Br•. A comparison with the selectivities of other radicals is given in ref. 20.

The activation parameters for the neopentane/methylene chloride competition were determined for the glutarimidyl radical (G•) and the phthalimidyl radical (P•) (Table 4).[20,23] The hydrogen abstraction competitions show little temperature dependence as a consequence of small, compensating activation parameters. This is an instance where the reactivity differences are not dominated by the $\Delta\Delta H^{\ddagger}$ term; the $T\Delta\Delta S^{\ddagger}$ is similar in magnitude and suggests an early transition state.[24]

3. Alkene Additions

If radical chain reactions with imidyl radicals are carried out under conditions where more alkene is present than in experiments where it only serves as a halogen scavenger, 1:1-addition becomes the major reaction.[8,13,14] The imidyl radical adds to an alkene forming an adduct radical which then reacts with N-haloimide to form the 1:1-addition product.

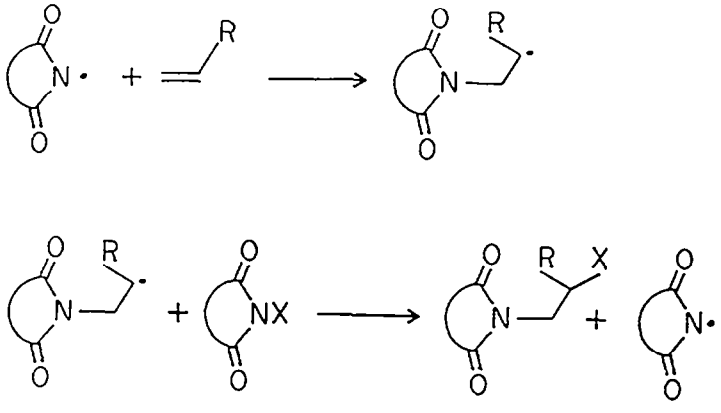


Table 5 summarizes the yields of some addition products formed in non-optimized reactions of N-bromo-3,3-dimethylglutarimide (33DMNBG) and N-bromophthalimide (NBP) with alkenes.

Table 5

Yields of 1:1 addition products[14] formed by reaction of 33DMNBG and NBP with various alkenes.[a)]

	DMNBG	NBP
ethylene	82%	---
t-butylethylene	83%	41%[b)]
isobutene	90%	53%
vinylacetate	80%	30-40%[b)]
2-chloropropene	89%	30-40%[b)]

a) All yields were determined by NMR in the reaction mixtures, except
b) Yields of purified products.

The addition reactions are remarkably clean reactions with high chain length (up to 2000)[14] which can be rationalized as follows. Imidyl radicals show electrophilic behavior by adding easily to electron rich alkenes forming adduct radicals. These nucleophilic alkyl radicals[26] abstract bromine from the N-bromoimides, thus regenerating the chain carrier. The alternation between electrophilic imidyl and nucleophilic alkyl radicals explains the high yields of the addition reactions. Electrophilic imidyl radicals prefer the addition to electron-rich alkenes, while nucleophilic alkyl radicals prefer the reaction with the N-haloimide. This also explains why the addition reaction does not preclude polymerization of less electron rich alkenes such as 1,1-dichloro-ethylene, and why no addition product is obtained with electron poor alkenes such as fumarodinitrile, maleic anhydride or tetrachloroethylene.[14] Styrene provides an intramolecular competition between addition to the double bond and addition to the aromatic nucleus, with the double bond being only twice as reactive as the benzene ring.[13]

Competition reactions between various alkenes show only small differences in rates of addition, a range of 3 with the alkenes shown in Table 5. Addition/abstraction competitions[11,14,23] carried out with neopentane and t-butylethylene, showed that glutarimidyl radicals add to alkenes ~100x faster than abstraction of a primary hydrogen atom (Table 6). The phthalimidyl radical adds to a double bond 10^3 times faster than it abstracts a primary hydrogen atom. Stabilization by the aromatic moiety may explain this difference.

This radical chain addition of N-haloimides to alkenes is an excellent synthetic reaction, resulting in the introduction of X and N at vicinal positions.

Table 6

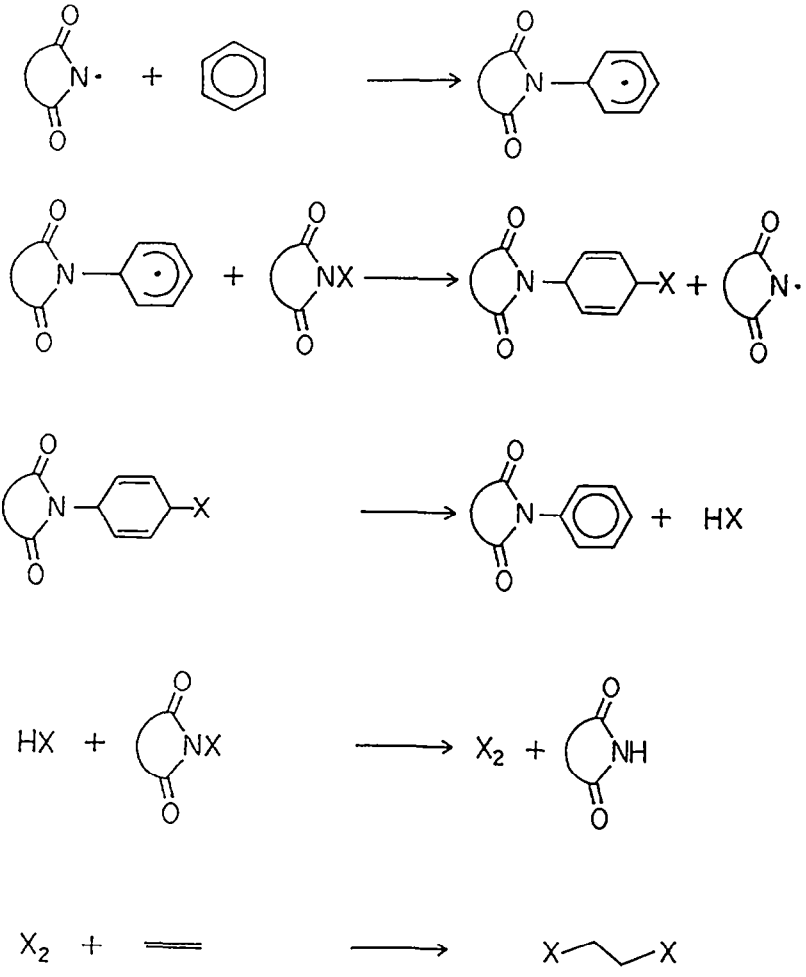
Selectivities of imidyl radicals in addition/abstraction competitions, carried out with t-butylethylene and neopentane.[a)]

	S•c)	G•d)	P•e)	Cl•b)
addition/ abstraction[a]	~80	~100	~1000	58

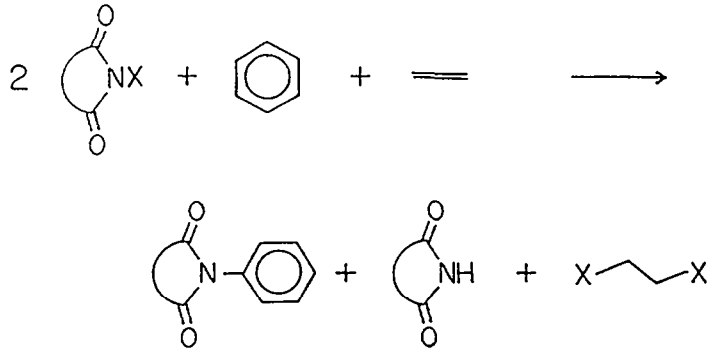
a) The selectivities are calculated on a per double bond and per hydrogen basis. S•, G• and P• stand for succinimidyl, glutarimidyl and phthalimidyl radicals. b) Calculated using 1-butene, ref. 27.
c) ref. 11. d) ref. 14. e) ref. 23.

4. Reactions with Arenes

Imidyl radicals also react with arenes. An addition/elimination sequence leads to substitution of the aromatic nucleus by an imidyl moiety. Imidyl radicals add to benzene with a rate similar to the rate of addition to alkenes,[14,15] forming a cyclohexadienyl radical. In strong contrast, the methyl radical strongly prefers alkenes (ethylene by a factor of approximately 100).[8,28] The cyclohexadienyl radical abstracts a halogen atom from the N-haloimide to give a cyclohexadiene (isomers are possible), which then loses HX to give the substituted arene. HX is scavenged by the N-haloimide giving imide and halogen. To ensure halogen-free reaction conditions, these reactions must be carried out with an alkene/N-haloimide ratio of at least 0.5. The intermediacy of a cyclohexadiene is indicated by the isolation of the tribromide formed by addition of Br_2,[29] especially noticeable when the scavenging by alkene is not efficient.



This mechanism is supported by the observed 1:1:1 stoichiometry for N-phenylimide, imide and dihaloalkane. At 70°C this is a clean reaction, but at lower temperatures side reactions such as halogen scavenging by the diene also occur (leading to N-(tribromocyclohexenyl)-imides).[15,29]



The overall rate of these benzene substitution reactions is small in comparison to alkene-additions or hydrogen abstractions. The slow step in the chain sequence must be the transfer of Br from the bromoimide to the cyclohexadienyl radical, since the adition step is irreversible and is as fast as addition to alkenes.[14] The irreversibility of the addition to benzene is indicated by the non-dependence of the relative rate constants for additions to alkenes and benzene (direct competition) on the concentrations of alkene, benzene or N-bromoimide.[14]

The reaction of imidyl radicals with arenes also indicates the electrophilic character of imidyl radicals. As found with ·OH, benzene/alkene competition rate constants are close to unity[8] (OH· = 4.3, S·=2.0, G·=0.5), whereas for nucleophilic radicals such as the methyl there is a preference for addition to ethylene by a factor of ~100.[8,28]

ABSOLUTE RATE CONSTANTS FOR IMIDYL RADICAL REACTIONS

Absolute rate constants for imidyl radical reactions have been determined in three different types of experiment: flash photolysis of 33DMNBG in cyclohexane at 25°C,[30] benzoyl peroxide initiated substitution of cyclohexane by NBS at 50°C[12] and di-tert.-butylperoxyoxalate initiated addition of 33DMNBG to alkenes at 35°C.[14]

Table 7

Minimum absolute rate constants for the reaction of N-centered radicals with cyclohexane.
$N\cdot + c\text{-}C_6H_{12} \rightarrow NH + C_6H_{11}\cdot$

Radical	T/°C	$k(M^{-1}sec^{-1})$	ref.
	35	$>10^5$ a)	14
	25	$>3.5 \times 10^3$ b)	30
	50	$>10^4$ c)	12
	28	$>6.4 \times 10^3$ d)	31

a) Calculated from the absolute rate constant of addition to ethene (peroxide catalyzed) and the relative rate constants for the cyclohexane/ethene competition (0.55). b) Flash photolysis of 33DMNBG. c) Benzoyl peroxide catalyzed. d) Tert.-butyl hyponitrite catalyzed.

In Table 7 the results are summarized, with all measurements normalized to H-abstraction from cyclohexane, by using the relative rates. The differences between the rate constants are attributed to the difficulties in determining absolute rate constants for radical chain reactions by chain length measurements. In each instance these values must be regarded as minimum values. Reactions with high chain lengths (400-2000 for the addition reactions,[14] up to 8000 for the bromination of cyclohexane by NBS[12]) are more sensitive to the effects of small amounts of inhibitors. Therefore it is more likely that the absolute rate constant for the substitution of cyclohexane is in the range of 10^5 M^{-1} sec^{-1} or higher. For the ring-opening reaction of the succinimidyl radical a rate constant of $10^7 M^{-1}sec^{-1}$ had been suggested,[11] based on the assumption of an encounter-controlled rate constant for alkyl radicals with Br_2. The current crop of absolute rate constants fall short of this value. One can conclude tentatively that despite the similarity of substitution selectivities, Cl· reacts faster in hydrogen abstractions by 4-5 powers of ten.[22,32]

ELECTROCHEMICAL REDUCTION OF N-HALOIMIDES

Ross and Eberson[33] have studied the electrochemical reductions of NBS and NCS. One electron per molecule of NXS is used in this reduction which has proved to be a rather complex reaction sequence, involving the formation of succinimidyl anion (S^-) as an intermediate. It is suggested that the succinimidyl anion reacts with NXS to form two imidyl radicals plus a halogen anion. The reaction products are not well characterized, but in a number of reactions the imide (SH) and maleinimide (isolated as polymaleinimide) are formed in a ratio close to unity. The formation of the imide and maleinimide (MH) is attributed to a disproportionation of two succinimidyl radicals ($S^\bullet$); the maleinimide then undergoes a radical polymerization. Scheme II shows a simplified version of their mechanism for the electrochemical reduction of NXS.

Scheme II

$$NXS + 2e^- \rightarrow S^- + X^-$$

$$S^- + NXS \rightarrow 2S^\bullet + X^-$$

$$2S^\bullet \rightarrow SH + MH$$

$$MH \xrightarrow{\text{radical}} \text{polymaleinimide}$$

σ/π

For imidyl radicals, as well as for others, two possible states must be considered, as indicated by a σ-and a π-structure.[34,35,36] The σ-structure is characterized by an odd electron located in an sp^2 orbital of the nitrogen, thus having 6 electrons in the delocalized π-system. The π-structure is characterized by 5 electrons in the conjugated system and an electron pair in the sp^2 orbital.

A series of attempts[8,11,16,37] was directed toward gaining access to both of these radicals via thermal reactions, and success was claimed. But re-examination of this field[17,18] shows that in most cases the chemistry could be explained with only one imidyl radical and other competing reactions.

An ESR-spectrum of an x-irradiated succinimide crystal[38] and ab initio calculations[39,40] show the π to be the ground state. The energy differences to the first excited σ-state were calculated to be 21.5 kJ/mol[39] and 49.0 kJ/mol.[40] However, orbital symmetry considerations and MNDO calculations[41] indicate the ring-opening reaction of the succinimidyl radical should be a "forbidden" reaction for the π-state because the π-orbital and the bond being broken are orthogonal to one another.[34] To date it is not clear whether this "forbidden" ring-opening of a π-radical occurs and thus all of the chemistry described above is to be attributed to the π state, or whether it is only the σ-radical that ring opens, and that the chemistry described in the preceding sections is attributable to the σ excited state, leaving the chemistry of the ground state unknown at present.

SUMMARY

The attempts to explain the Ziegler bromination and the search for σ-and π-radicals opened a new field in radical chemistry: the chemistry of imidyl radicals, showing unexpected behavior in substitution and addition reactions. At present there is evidence for only one imidyl radical and the assignment of the chemistry to a π or a σ state remains unsettled.

ACKNOWLEDGMENT

This work was carried out with financial support from The National Science Foundation. U. L. thanks the Alexander von Humboldt Foundation for a partial stipendium from the Lynen Fund.

References

1. K. Ziegler, A. Späth, E. Schaaf, W. Schumann, E. Winkelmann, Liebigs Ann. Chem. 551 (1942) 80.
2. G. F. Bloomfield, J. Chem. Soc. 1944 114.
3. a) J. Adam, P. A. Gosselain, P. Goldfinger, Nature (London) 171 (1953) 704.
   b) P. A. Gosselain, J. Adam, P. Goldfinger, Bull. Soc. Chim. Belg. 65 (1956) 533.
4. In non-polar solvents Br_2-addition to alkenes occurs in a third order reaction $r=k[=][Br_2]^2$, P.B.D. de la Mare, R. D. Wilson, J. Chem. Soc. Perkins II 1977 2048.
5. a) F. L. J. Sixma, R. H. Reim, Koninkl. Ned. Akad. Wetenschap. Proc. 1958, B61, 183.
   b) B. P. McGrath, J. M. Tedder, Proc. Chem. Soc. (London) 1961, 80.
   c) R. E. Pearson, J. C. Martin, J. Am. Chem. Soc. 85 (1963) 354, 3142.
   d) G. A. Russell, C. DeBoer, K. M. Desmond, J. Am. Chem. Soc. 85 (1963) 365, 3139.
   e) C. Walling, A. L. Rieger, D. D. Tanner, J. Am. Chem. Soc. 85 (1963) 3129.
   f) J. H. Incremona, J. C. Martin, J. Am. Chem. Soc. 92 (1970) 627.
   g) W. A. Thaler in "Methods in Free Radical Chemistry." V. 2; E. S. Huyser, Ed., Marcel Dekker: New York 1969; p. 198.
6. J. C. Day, M. J. Lindstrom, P. S. Skell, J. Am. Chem. Soc. 96 (1974) 5616.
7. J. G. Traynham, Y. S. Lee, J. Am. Chem. Soc. 96 (1974) 3590.
8. P. S. Skell, J. C. Day, Acc. Chem. Res. 11 (1978) 381.
9. a) J. C. Martin, P. D. Bartlett, J. Am. Chem. Soc. 79 (1957) 2533.
   b) H. W. Johnson, D. E. Bublitz, J. Am. Chem. Soc. 80 (1958) 3150.
10. a) G. R. Chalfont, M. J. Perkins, A. Horsfield, J. Chem. Soc. B 1970, 401.
    b) C. Lagercrantz, S. Forshult, Acta Chim. Scand. 23 (1969) 708.
11. R. L. Tlumak, J. C. Day, J. P. Slanga, P. S. Skell, J. Am. Chem. Soc. 104 (1982) 7257.
12. C. Walling, G. M. El-Taliawi, C. Zhao, J. Am. Chem. Soc. 105 (1983) 5119.
13. J. C. Day, M. G. Katsaros, W. D. Kocher, A. E. Scott, P. S. Skell J. Am. Chem. Soc. 100 (1978) 1950.
14. U. Lüning, D. S. McBain, P. S. Skell, submitted to the J. Am. Chem. Soc.
15. U. Lüning, P. S. Skell, submitted to the J. Am. Chem. Soc.
16. P. S. Skell, R. L. Tlumak, S. Seshadri, J. Am. Chem. Soc. 105 (1983) 5125.
17. P. S. Skell, U. Lüning, D. S. McBain, J. M. Tanko, submitted to the J. Am. Chem. Soc.
18. D. D. Tanner, D. W. Reed, S. L. Tan, C. P. Meintzer, C. Walling, A. Sopchik, private communication, submitted to the J. Am. Chem. Soc.
19. Y. L. Chow, Y. M. A. Naguib, J. Am. Chem. Soc. 106 (1984) 7557.
20. U. Lüning, S. Seshadri, P. S. Skell, submitted to the J. Am. Chem. Soc.

21. G. A. Russell, J. Am. Chem. Soc. 80 (1958) 4997.
22. G. C. Fettis, J. H. Knox, Prog. React. Kinet 2 (1964) 3.
23. D. S. McBain, P. S. Skell, to be submitted to the J. Am. Chem. Soc.
24. a) P. S. Skell, M. S. Cholod, J. Am. Chem. Soc. 91 (1969) 7131.
b) B. Giese, Acc. Chem. Res. 17 (1984) 438.
25. W. Thaler, J. Am. Chem. Soc. 85 (1963) 2607.
26. B. Giese, Angew. Chem. 95 (1983) 771.
27. M. L. Poutsma, J. Am. Chem. Soc. 87 (1965) 2172.
28. Landolt-Börnstein, New Series, Group II, Vol. 13b, p. 78, Ed.: H. Fischer, Springer Berlin 1984.
29. F.-L. Lu, Y. M. A. Naguib, M. Kitadani, Y. L. Chow, Can. J. Chem. 57 (1979) 1967.
30. R. W. Yip, Y. L. Chow, C. Beddard, J. Chem. Soc., Chem. Commun. 1981 955.
31. R. Sutcliffe, M. Anpo, A. Stolow, K. U. Ingold, J. Am. Chem. Soc. 104 (1982) 6064.
32. M. L. Poutsma in "Methods in Free-Radical Chemistry," Ed.: E. S. Huyser, Marcel Dekker, Publisher: New York, 1969, p. 84.
33. a) J. E. Barry, M. Finkelstein, W. M. Moore, S. D. Ross, L. Eberson, L. Jönsson, J. Org. Chem. 47 (1982) 1292.
b) J. E. Barry, M. Finkelstein, W. M. Moore, S. D. Ross, L. Eberson, Tetrahedron Lett. 25 (1984) 2847.
c) L. Eberson, J. E. Barry, M. Finkelstein, W. M. Moore, S. D. Ross, Acta Chem. Scand. Ser B., in press.
d) J. E. Barry, M. Finkelstein, W. M. Moore, S. D. Ross, L. Eberson, J. Org. Chem. 50 (1985) 528.
34. T. Koenig, A. Wielesek, Tetrahedron Lett. 1975, 2007.
35. E. Hedaya, R. L. Hinman, U. Schomaker, S. Theodoropulos, L. M. Kyle, J. Am. Chem. Soc. 89 (1967) 4875.
36. M. J. S. Dewar, A. H. Pakiari, A. B. Pierini, J. Am. Chem. Soc. 104 (1982) 3242.
37. a) R. L. Tlumak, P. S. Skell, J. Am. Chem. Soc. 104 (1982) 7267.
b) P. S. Skell, J. C. Day, J. Am. Chem. Soc. 100 (1978) 1951.
c) P. S. Skell, J. C. Day, J. P. Slanga, Angew. Chem. Int. Ed. Engl. 17 (1978) 515.
d) P. S. Skell, S. Seshadri, J. Org. Chem. 49 (1984) 1650.
e) P. S. Skell, J. Am. Chem. Soc. 106 (1984) 1838.
38. A. Lund, P. O. Samskog, L. Eberson, S. Lunell, J. Phys. Chem. 86 (1982) 2458.
39. M. J. Field, I. H. Hillier, S. A. Pope, M. F. Guest, J. Chem. Soc., Chem. Commun. 1985, 219 and references cited therein.
40. C. Petrongolo, S. D. Peyerimhoff, private communication, submitted to the J. Am. Chem. Soc.
41. M.J.S. Dewar, S. Olivella, J. Chem. Soc., Chem. Commun. 1985, 301.