^{1}H NMR (CDCl$_3$, δ) 1.70 (d, 3 H, J = 3 Hz), 2.18 (t, 2 H, J = 3 Hz), 2.75 (q, 2 H, J = 3 Hz), 4.20 (m, 1 H). Reaction of the isocyanate with methanol gives methyl *N*-(4-bromopentanoyl)carbamate: mp 94-96 °C, ^{1}H NMR (CDCl$_3$, δ) 1.75 (d, 3 H, J = 3 Hz), 2.30 (t, 2 H, J = 3 Hz), 2.95 (q, 2 H, J = 3 Hz), 3.75 (s, 3 H), 4.20 (m, 1 H), 8.1 (br, 1 H).

Competition Reactions. All reactions were carried out in 30-mL-capacity Pyrex pressure tubes containing Teflon-coated stir bars, sealed with o-ringed Teflon needle valves. Reactant mixtures were degassed 2-5 times by a freeze-pump-thaw technique with freezing and evacuating at −196 °C and thawing at room temperature. The sealed pressure tube was placed in a temperature-controlled water bath for either peroxide or light initiation. Irradiation was through two layers of Pyrex with a 400-W medium pressure mercury arc at a distance of 5-15 cm, for 0.75-5 h (reaction at 15 °C).

At the completion of a reaction, the volatile materials were separated from the nonvolatiles by high vacuum trap-to-trap distillation. The nonvolatiles were examined by ^{1}H NMR, and the product yields were obtained by direct integrations employing an internal standard (hexamethyldisiloxane). The amount of unreacted *N*-halo imide was also determined iodometrically with an aliquot of the nonvolatiles. The volatile portion of the products was characterized either by gas chromatography subsequent to addition of an internal standard (chlorobenzene or carbon tetrachloride) or by ^{1}H NMR employing an internal standard (hexamethyldisiloxane). Products were identified by comparison of gas chromatography retention times and/or spectra with those of authentic samples.

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.

Registry No. NBS, 128-08-5; *t*-BuOOH, 75-91-2; $(CH_3)_3CCH{=}CH_2$, 558-37-2; $(CH_3)_2CBr(CH_2)_2C(O)NCO$, 82621-92-9; $(CH_3)_2CBr(CH_2)_2C(O)NHC(O)OMe$, 82621-93-0; $CH_3CHBr(CH_2)_2C(O)NCO$, 82621-95-2; $CH_3CHBr(CH_2)_2C(O)NHC(O)OMe$, 82621-96-3; CH_2Cl_2, 75-09-2; $CH_2{=}CCl_2$, 75-35-4; $(CH_3)_2CHCH(CH_3)_2$, 79-29-8; EtPh, 100-41-4; MePh, 108-88-3; 2,2-dimethylglutaric anhydride, 2938-48-9; 2,2-dimethylglutarimide, 1194-33-8; 2-methylglutarimide, 29553-51-3; *N*-bromo-2,2-dimethylglutarimide, 82621-80-5; *N*-bromo-2-methylglutarimide, 82621-79-2; *N*-bromoglutarimide, 3699-18-1; *N*-bromo-3,3-dimethylglutarimide, 66393-63-3; *N*-chloro-3,3-dimethylglutarimide, 82621-83-8; 3,3-dimethylglutarimide, 1123-40-6; oxalyl chloride, 79-37-8; di-*tert*-butyl peroxyoxylate, 1876-22-8; neopentane, 463-82-1; ethene, 74-85-1; butane, 106-97-8; 2-norbornene, 498-66-8; 1,3-butadiene, 106-99-0.

Free Radical Addition of *N*-Bromoglutarimides and *N*-Bromophthalimide to Alkenes. Absolute and Relative Rates

Ulrich Lüning, Douglas S. McBain, and Philip S. Skell*

Department of Chemistry, The Pennsylvania State University, University Park, Pennsylvania 16802

Received October 10, 1985

N-Bromoglutarimides and *N*-bromophthalimide add to electron-rich alkenes, in free radical chain reactions, with yields up to 90%, thus effecting vicinal additions of halogen and amino functions. Relative rates for the addition of *N*-bromo-3,3-dimethylglutarimide (**1a**) and *N*-bromophthalimide (**1b**) to different alkenes show little rate discrimination among electron-rich alkenes, but these imides do not add to electron-deficient alkenes such as maleic anhydride and tetrachloroethylene. A minimum value of the absolute rate constant for the addition step is 10^5 L/mol s at 35 °C. These reactions have good synthesis potential, even with alkenes which would undergo allylic substitution under Ziegler conditions.

The major evidence for the recognition of imidyl radicals as reaction intermediates has depended on substitution reactions with reagents such as *N*-bromosuccinimide (NBS) which replaces H by Br in the substrate.[1] Since the imidyl moiety does not surface as a part of this product, substitution reactions do not provide definitive evidence for the intermediacy of imidyl radicals, such as one obtains from addition reactions.

The small amounts of additions to alkenes of *N*-halo imides, noted by Ziegler and co-workers,[2] have been attributed to the intrusion of ionic processes. Only with tetrafluoro-*N*-bromosuccinimide[3] was this reported to be a major pathway.

We describe here the evidence that the additions are chain reactions inhibited by oxygen, that imidyl radicals are the carriers which add to the alkenes, that imidyls show little discrimination among differently substituted electron-rich alkenes, and that the rate of each step in the addition must be greater than 10^5 M^{-1} s^{-1}. These reactions would be useful in syntheses that would require the additions of amino and halo fragments to alkenes.

The radical chain additions of *N*-bromo imides **1** to alkenes can be photo or peroxide initiated.[3] In these reactions the alkenes serve as both substrate and scavenger of the small amounts of Br· and Br$_2$ that are produced. Radical chain additions of *N*-bromosuccinimide (NBS) and other *N*-halo imides to alkenes provided unambiguous proof of the intermediacy of imidyl radicals. These high yield reactions largely escaped notice over the preceding four decades because reactions of NBS were mainly restricted to carbon tetrachloride as the solvent,[2] to effect allylic brominations. The low solubility of NBS in carbon tetrachloride ($\sim 10^{-3}$ M) precluded the operation of the imidyl chain.[4] The addition to alkenes is a major reaction channel if the *N*-halo imide is soluble.[1a] Better solubility

---

[1] (a) Day, J. C.; Katsaros, M. G.; Kocher, W. D.; Scott, A. E.; Skell, P. S. *J. Am. Chem. Soc.* **1978**, *100*, 1950. (b) Skell, P. S.; Day, J. C. *Acc. Chem. Res.* **1978**, *11*, 381.

[2] Ziegler, K.; Späth, A.; Schaaf, E.; Schumann, W.; Winkelmann, E. *Justus Liebigs Ann. Chem.* **1942**, *551*, 80.

[3] Pearson, R. E.; Martin, J. C. *J. Am. Chem. Soc.* **1963**, *85*, 354, 3142.

[4] Day, J. C.; Lindstrom, M. J.; Skell, P. S. *J. Am. Chem. Soc.* **1974**, *96*, 5616.

0022-3263/86/1951-2077$01.50/0 © 1986 American Chemical Society

Table I. Reaction Conditions for the Synthesis of *N*-(2-Bromoalkyl)-3,3-dimethylglutarimides

5	33DMNBG[b]	solvent[c]	alkene **3**[b]	irradtn time[d] (min)	yield[a] (%)
a *N*-(2-bromoethyl)-3,3-dimethylglutarimide	2.14	10 CCl_4	3.8 ethene	210	82
e *N*-(2-bromo-3,3-dimethylbutyl)-3,3-dimethylglutarimide	0.90	5 CH_2Cl_2	3.1 3,3-dimethyl-1-butene	45	83
d *N*-(2-bromo-2-methylpropyl)-3,3-dimethylglutarimide	0.98	5 CH_2Cl_2	6.1 isobutene	90	90
b *N*-(2-acetoxy-2-bromoethyl)-3,3-dimethylglutarimide	0.89	5 CH_2Cl_2	5.4 vinyl acetate	35	80
c *N*-(2-bromo-2-chloropropyl)-3,3-dimethylglutarimide	1.05	5 CH_2Cl_2	5.9 2-chloropropene	30	89

[a] Yields determined by NMR. [b] mmol. [c] mL. [d] UV irradiation with a 400-W mercury arc through Pyrex at 13 °C at a distance of 5 cm.

Table II. Reaction Conditions for the Synthesis of *N*-(2-Bromoalkyl)phthalimides

5	NBP[a]	alkene **3**[a]	irradtn time[c] h	yield[d] (%)
f *N*-(2-bromo-3,3-dimethylbutyl)phthalimide	3.1[b]	3.9 3,3-dimethyl-1-butene	5.3	41[e]
g *N*-(2-bromo-2-methylpropyl)phthalimide	2.4[b]	5.1 isobutene	5.3	53[f]
h *N*-(2-acetoxy-2-bromoethyl)phthalimide	1.9[g]	5.4 vinyl acetate	2.3	30–40[e]
i *N*-(2-bromo-2-chloropropyl)phthalimide	1.6[g]	5.9 2-chloropropene	8	30–40[e]

[a] mmol. [b] In 5 mL of CH_2Cl_2. [c] UV irradiation with a 400-W mercury arc through Pyrex at 13 °C at a distance of 5 cm. [d] Based on initial NBP. [e] Purified. [f] Crude yield. [g] In 2 mL of CH_2Cl_2.

Table III. Physical Data for *N*-(2-Bromoalkyl)-3,3-dimethylglutarimides 5a–e

5	mp (°C)	NMR	MS, *m/e* (relative intensity)
a $C_9H_{14}BrNO_2$ (248.13)	57	1.12 (s, 6 H), 2.55 (s, 4 H), 3.51 (t, *J* = 6.7 Hz, 2 H), 4.22 (t, *J* = 6.7 Hz, 2 H)	249, 247 (20, 20 M^+), 168 (86, $M^+ - Br$), 83 (100, $Me_2C{=}CH^+CO$)
b $C_{11}H_{16}BrNO_4$ (306.16)	78	1.09 (s, 6 H), 2.09 (s, 3 H), 2.54 (s, 4 H), 4.41 (mc, 2 H), 6.78 (mc, 1 H)	307, 305 (1, 1, M^+), 264, 262 (12, 12, $M^+ - CH_3CO$), 226 (27, $M^+ - Br$), 184 (100, $GCH_2{}^+CHOH$)
c $C_{10}H_{15}BrClNO_2$ (296.60)	72–73	1.14 (s, 6 H), 2.25 (s, 3 H), 2.59 (s, 4 H), 4.62 (d, *J* = 7.0 Hz, 1 H), 4.73 (d, *J* = 7.0 Hz, 1 H)	262, 260 (0.7, 0.6, $M^+ - Cl$), 218, 216 (25, 76, $M^+ - Br$), 83 (100, $Me_2C{=}CH^+CO$)
d $C_{11}H_{18}BrNO_2$ (276.18)	75	1.12 (s, 6 H), 1.72 (s, 6 H), 2.56 (s, 4 H); 4.27 (s, 2 H)	276, 274 (<1, $M^+ - H$), 196 (100, $M^+ - Br$)
e $C_{13}H_{22}BrNO_2$ (304.23)	90	1.13 (1.14 (2 s, 15 H), 2.54 (s, 4 H), 3.86 (d, d, *J* = 2.4 Hz, *J* = 11.4 Hz, 1 H), 4.34 (d, d, *J* = 2.3 Hz, *J* = 11.4 Hz, 1 H), 4.56 (d, d, *J* = 11.3 Hz, *J* = 11.3 Hz, 1 H)	305, 303 (8, 8, M^+), 249, 247 (11, 12, $M^+ - C_4H_8$), 224 (81, $M^+ - Br$), 142 (100, $M^+ - C_6H_{10}Br$)

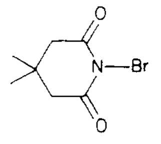
Table IV. Physical Data for *N*-(2-Bromoalkyl)phthalimides 5f–i

5	mp (°C)	NMR	MS, *m/e* (relative intensity)
f $C_{14}H_{16}BrNO_2$ (310.20)	78–81	1.13 (s, 9 H), 3.89 (d, d, *J* = 2.8 Hz, *J* = 14.2 Hz, 1 H), 4.11 (d, d, *J* = 11.1 Hz, *J* = 14.0 Hz, 1 H), 4.36 (nd, d, *J* = 11.2 Hz, *J* = 2.8 Hz, 1 H), 7.73 (m, 4 H)	311, 309 (13, 13, M^+), 230 (16, $M^+ - Br$), 160 (100, $M^+ - C_5H_{10}Br$)
g $C_{12}H_{12}BrNO_2$ (282.14)	93–95	1.81 (s, 6 H), 4.09 (s, 2 H), 7.82 (m, 4 H)	283, 281 (<1, <1, M^+), 202 (95, $M^+ - Br$), 160 (100, $M^+ - C_3H_6Br$)
h $C_{12}H_{10}BrNO_4$ (312.12)	130–134	210 (s, 3 H), 4.30 (mc, 2 H), 6.82 (mc, 1 H), 7.84 (m, 4 H)	232 (14, $M^+ - Br$), 190 (72, $M^+ - C_2H_2OBr$), 160 (82, $M^+ - C_3H_4O_2Br$), 43 (100, $M^+ - C_{10}H_5NO_3Br$)
i $C_{11}H_9BrClNO_2$ (302.56)	113–118	2.35 (s, 3 H); 4.41 (s, 2 H), 2 H, 7.85 (m, 4 H)	222 (16, $M^+ - Br$), 160 (100, $M^+ - C_2H_2BrCl$)

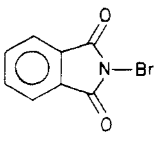
is achieved either with structure change such as introduction of alkyl groups in the imidyl backbone or by the use of better solvents such as methylene chloride or acetonitrile.

In the initiation step the nitrogen–bromine bond of the *N*-bromo imide is cleaved homolytically by irradiation, or a bromine atom is abstracted by a radical formed in the thermal decomposition of a peroxide or a peroxy ester. The imidyl radical formed in the initiation step adds to the double bond of an alkene. Bromine abstraction by the adduct radical **4** from the bromo imide leads to the 1:1 addition product **5** and regenerates the chain carrier.

We investigated this free-radical addition using *N*-bromo-3,3-dimethylglutarimide, 33DMNBG (**1a**), and *N*-bromophthalimide, NBP (**1b**), because this glutarimidyl and the phthalimidyl radicals show no tendency to undergo the ring-opening reaction, which is often a major competitive process for the succinimidyl radical derived from NBS.



1a



1b

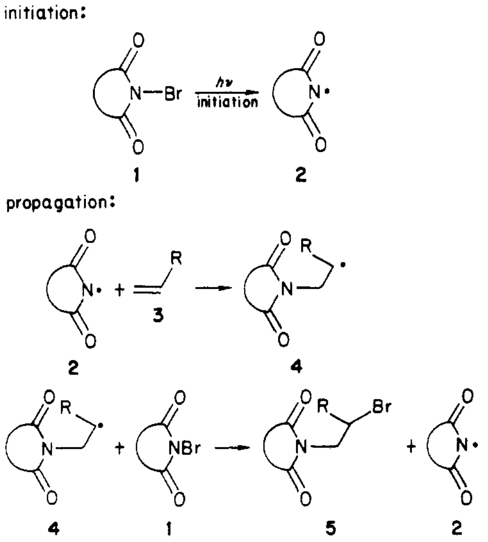


Table V. Alkene Competition Reactions for the 3,3-Dimethylglutarimidyl Radical 2a[a]

olefins[b]	solvents	r^c
3,3-dimethyl-1-butene/isobutene	CH_2Cl_2	0.72[e]
vinyl acetate/isobutene	CH_2C_2	1.6[d]
vinyl acetate/isobutene	CH_2Cl_2/C_6H_6	1.7[d]
vinyl acetate/2-chloropropene	CH_2Cl_2	1.1[d]
vinyl acetate/2-chloropropene	CH_2C_2/C_6H_6	1.1[d]
ethene[g]/3,3-dimethyl-1-butene	CC_4[f]	2.8[e]

[a] 0.14–0.19 M 22DMNBG. [b] Concentrations from 0.8–1.8 M. [c] Relative rate constant: mole ratio products/mole ratio reactants. [d] Analysis by 60-MHz NMR. [e] Analysis by 200-MHz NMR. [f] Inhomogeneous mixture. [g] 2.7 mmol of ethene, 5 mL of CH_2Cl_2, 30-mL capacity pressure tube, applying Henry's law ($k = 1.3 \times 10^{-7}$ m^2/N).[11] The ethene concentration in solution was calculated to be approximately 0.2 M.

Table VI. Alkene Competition Reactions for the Phthalimidyl Radical 2b[a]

olefins[b]	solvents	r^c
3,3-dimethyl-1-butene/isobutene	CH_2Cl_2	0.39
vinyl acetate/isobutene	CH_2Cl_2	0.43
vinyl acetate/isobutene	CH_2Cl_2/C_1H_6	0.47
vinyl acetate/2-chloropropene	CH_2Cl_2	1.3
vinyl acetate/2-chloropropene	CH_2Cl_2/C_6H_6	1.2
3,3-dimethyl-1-butene/2-chloropropene	CH_2Cl_2	1.1

[a] Heterogeneous reaction conditions throughout 1.8–2.2 mmol of NBP in 3–4 Ml of solvent. [b] Concentrations from 1.1–3.9 M. [c] Relative rate constants: mole ratio products/mole ratio reactants.

Table VII. Relative Rate Constants for the Addition of 3,3-Dimethylglutarimidyl Radicals 2a to Alkenes (r(isobutene) ≡ 1.0)

alkene	r
3a ethene	2
3b vinyl acetate	1.7
3c 2-chloropropene	1.6
3d isobutene	≡1.0
3e 3,3-dimethyl-1-butene	0.7
benzene[a]	0.5
1,1-dichloroethene	polymerizes
fumarodinitrile	
maleic anhydride	
tetrachloroethene	

[a] Per molecule.

Table VIII. Relative Rate Constants for the Additions of Phthalimidyl Radicals 2b to Alkenes (r(isobutene) ≡ 1.0)

alkene	r
3d isobutene	1.0
3b vinyl acetate	0.4
3e 3,3-dimethyl-1-butene	0.4
3c 2-chloropropene	0.3
1,1-dichloroethene	polymerizes

Synthesis. UV light initiation of *N*-bromo-3,3-dimethylglutarimide, 33DMNBG (**1a**), or *N*-bromophthalimide, NBP (**1b**), results in additions to a variety of alkenes, in unoptimized yields as large as 90%. The yields and reaction conditions are listed in Tables I and II; the physical data for the addition products **5** are listed in Tables III and IV. These reactions have long chain lengths (see below). For example, the addition of 33DMNBG (**1a**) to vinyl acetate is initiated satisfactorily by ambient hood lighting (100% conversion in 2 h at 15 °C), and it is strongly inhibited by oxygen.

This type of reaction effects simultaneous vicinal addition of amino and halo functions to an alkene in good yield.

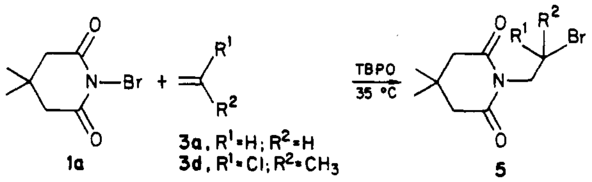
Competition Reactions. Competitions for the addition of imidyl radicals **2** to different alkenes **3** were carried out for 3,3-dimethylglutarimidyl (**2a**) and phthalimidyl radicals (**2b**). Tables V and VI list the experimental conditions and results.

The range of relative rate constants of addition to electron-rich alkenes (Tables VII and VIII) is small. However, addition reactions failed for electron-poor alkenes such as fumarodinitrile, maleic anhydride, or tetrachloroethene; 1,1-dichloroethene was polymerized.

These results can be understood as follows: imidyl radicals show electrophilic behavior by adding easily to electron-rich alkenes forming adduct radicals **4**. These are alkyl radicals, and their nucleophilic[5] behavior avoids polymerization (the adduct radical of 1,1-dichloroethene is probably electrophilic). The adduct radicals abstract bromine from the *N*-bromo imides thus forming the electrophilic radicals chain carriers **2**. The alternation of electrophilic and nucleophilic radicals can explain the high yields of the addition reactions.

Relative rate constants for the abstraction of hydrogen atoms vs. the addition of 3,3-dimethylglutarimidyl radicals (**2a**) to double bonds were obtained from neopentane/3,3-dimethyl-1-butene competition experiments (Table IX). The addition to this double bond is 100 times faster than the abstraction of a primary hydrogen atom showing a behavior similar to that of S·(~80)[6] and Cl·(58).[7] For the phthalimidyl radical (**2b**) this selectivity was found to be 1000.[8] Since hydrogen abstractions by imidyl radicals operate with an early transition state, that is, they are not sensitive to the stability of the product radical, the addition is usually faster than the competitive allylic brominations which are the dominant reactions under Ziegler conditions (Br· chains).

Absolute Rate Constant of Addition to a Double Bond. To estimate the minimum absolute rate constants for the additions of the 3,3-dimethylglutarimidyl radical (**2a**) to alkenes, the additions of *N*-bromo-3,3-dimethylglutarimide (**1a**) to 2-chloropropene (**3d**) and ethene (**3a**)



were monitored by ^1H NMR. To initiate the reaction, di-*tert*-butyl peroxyoxalate (TBPO) was decomposed at

Table IX. 3,3-Dimethyl-1-butene/Neopentane Competition Experiments for Abstraction and Addition Reactions of the 3,3-Dimethylglutarimidyl Radical 2a

1a[a,b]	neo-C_5H_{12}[a]	3,3-dimethyl-1-butene **3e**[a]	irradtn time[c] (min)	$CHBrCl_2$[a]	$C_5H_{11}Br$[a]	**2e**[a]	k(neo-C_5H_{12}/$CH_2Cl_2)_H$[d]	$k(\mathbf{3e}/1°)_H$[e]
0.96	2.55	0.39	8	0.120	0.126	0.144	5.4	90
0.94	2.97	0.39	7	0.084	0.105	0.122	5.5	106
0.87	2.78	0.39	11	0.064	0.076	0.096	5.5	108

[a] mmol. [b] In 5 mL of CH_2Cl_2 at 14–15 °C. [c] UV-irradiation with a medium-pressure mercury arc through Pyrex at a distance of 5 cm. [d] Relative rate constant on a per hydrogen basis. [e] Relative rate constant on a per double bond per hydrogen basis.

Table X. NMR Data for TBPO-Catalyzed Radical Additions of *N*-Bromo-3,3-dimethylglutarimide (1a)

2-chloropropene (3d)					ethene (3a)				
t^a	[**1a**]^b	$-\frac{d[\mathbf{1a}]^c}{dt}$	[**3d**]^b	$k_{add}{}^d$	t^a	[**1a**]^b	$-\frac{d[\mathbf{1a}]^c}{dt}$	[**3a**]^b	$k_{add}{}^d$
0	0.2		0.23		0	0.156			
60^e	0.084	2.2×10^{-5}	0.11	4.9×10^4	12	0.10	8×10^{-5}	0.097	3.3×10^5
80	0.062	1.74×10^{-5}	0.09	4.9×10^4	20^f	0.062	5.9×10^{-5}	0.068	3.5×10^5
90	0.052	1.19×10^{-5}	0.08	3.8×10^4	28	0.037	3.6×10^{-5}	0.047	3.1×10^5
100	0.046	1.19×10^{-5}	0.08	3.9×10^4	36	0.022	2.7×10^{-5}	0.041	2.6×10^5
110	0.038	8.8×10^{-6}	0.07	3.4×10^4	44	0.011	2.3×10^{-5}	0.039	2.4×10^5
					52	0.003	1.1×10^{-5}	0.035	1.3×10^5

^{a}min. ^{b}mol/L. ^{c}mol/L·s; determined from graph. ^{d}L/mol·s. ^{e}[TBPO] at 60 min: 4.9×10^{-4} M; chain length for the time period (60–110 min): $\lambda = 422$. ^{f}[TBPO] at 20 min: 2.7×10^{-4} M; chain length for the time period (20–44 min): $\lambda = 2000$.

35 °C. The rate of this unimolecular decomposition is known:[9] $k_{dec} = 6.8 \times 10^{-5}\ s^{-1}$. Its decomposition, the disappearance of the bromo imide **1a**, and the formation of the addition product **5** could be followed with the integrated NMR signals. Table X lists the NMR data. After a short induction period, the TBPO decomposed at a rate in agreement with the known rate constant. The chain lengths were 400 for the experiment with 2-chloropropene (**3d**) and 2000 for ethene (**3a**). This chain reaction consists of two reaction steps: the addition of the imidyl radical to the alkene and the Br transfer from *N*-bromo-3,3-dimethylglutarimide to the adduct radical **4**. Estimates of the rate constant for the Br transfer[6] of $\sim 10^8\ M^{-1}\ s^{-1}$ indicate the addition reaction (reaction 2) is the slow step.

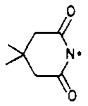
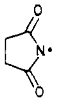
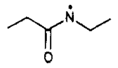
Therefore, equation (I)[10] was used to calculate the rate constant for the addition step, k_{add}. The assumptions for the use of this equation are

$$\frac{d[\mathbf{5}]}{dt} = -\frac{d[\mathbf{1a}]}{dt} = k_{add}\frac{k_{dec}[\text{TBPO}]^{1/2}}{2k_{term}}[\mathbf{3}] \qquad (I)$$

long chain lengths and one step of the reaction being slower than the other (the addition in this instance) and $k_{term} \simeq 10^9\ M^{-1}\ s^{-1}$. However, chain carriers can be lost to some cross coupling or to inhibitors. The rate of decomposition of TBPO was used in the calculation, without correction for those radicals which do not escape the cage. Thus, the k_{add} must be a minimum value. The values of k_{add} at 35 °C are $>4 \times 10^4\ M^{-1}\ s^{-1}$ (2-chloropropene) and $>3 \times 10^5\ M^{-1}\ s^{-1}$ (ethene); these are lower limits for the addition steps.

The absolute rate constant for the addition to a double bond, taken in connection with relative rate constants, allows the estimation of lower limits for other absolute rate constants (e.g., H abstraction from cyclohexane) and the comparison of those with values from the literature. In a cyclohexane/ethene competition experiment with 33DMNBG, the relative rate constant is $(k_{C_6H_{12}}/k_{C_2H_4}) = 0.55$ at 10 °C. Using $k_{C_2H_4} \geqslant 3 \times 10^5\ M^{-1}\ s^{-1}$, the absolute rate constant for the H abstraction from cyclohexane is $k_{C_6H_{12}} \geqslant 10^5\ M^{-1}\ s^{-1}$. A comparison with values from the literature (Table XI) shows differences of at least one order of magnitude, which cannot be explained by the different reaction temperatures (i.e., the rate constant obtained at 50 °C is *smaller* than the one at 35 °C). The variation in the values of Table XI shows that the absolute rate constants for these radical chain reactions should only be taken as approximations of the minimum values, attributable to the various problems attending the determination of absolute rates.

Table XI. Comparison of Absolute Rate Constants for the Reaction of N-Centered Radicals with Cyclohexane

radical	T (°C)	k (L/mol s)	ref^a
	35	$\geqslant 10^5$	this work
	25	>3500	12
	50	>10000	13
	28	>6400	14

^{a}These rates are shown as minimum values (see text).

Experimental Section

^{1}H NMR spectra were recorded on either a Varian EM-360 or a Bruker WH-200 spectrometer with chemical shifts reported on the δ-scale relative to hexamethyldisiloxane (δ = 0.07). Mass spectra were taken on a Kratos 9/50 at 70 eV. Gas chromatography analyses were carried out on a Hewlett-Packard HP 5790A FID with a DB-5 capillary column 30 m × 0.25 mm and a Hewlett-Packard 3390A integrator.

Materials. *N*-Bromo-3,3-dimethylglutarimide (**1a**) was purified by dissolving it in CH_2Cl_2 and crystallizing by addition of pentane. *N*-Bromophthalimide (**16**) was prepared as described.[8] Dichloromethane was distilled from phosphorus pentoxide, the middle cut was taken, and the purity was checked by GLC (≥99.99%). Benzene (Fisher) was purified by two recrystalization cycles and was dried with molecular sieves (≥99.98%). Cyclohexane (Aldrich) was run through aluminum oxide containing 4% silver nitrate and found to be 99.9% by GLC. Di-*tert*-butyl peroxyoxalate was prepared as described.[9] Tetrachloromethane (Fisher), 3,3-dimethyl-1-butene, vinyl acetate, 2-chloropropene, hexamethyldisiloxane (all Aldrich), ethene (Matheson, research grade, ≥99.99%), and isobutene (Matheson) were used without further purification.

Synthesis Procedure. Addition Products 5a–e. *N*-Bromo-3,3-dimethylglutarimide (**1a**), solvent, and alkene **3** were degassed in a 30-mL Pyrex pressure tube with a Teflon needle valve (O-rings) by using a thaw–freeze–pump technique 5 times. The homogeneous solutions (the run in CCl_4 was not homogeneous) were put in a 13 °C water bath and irradiated with a 400-W medium pressure mercury arc through Pyrex at a distance of 5 cm. Trap-to-trap distillation removed the volatiles and led to the crude addition products **5a–e**. The yields were determined by NMR. The products **5a–e** could be purified by dissolving them in tetrachloromethane or warm hexane and recrystallized by

---

(5) Giese, B. *Angew. Chem.* **1983**, *95*, 771.

(6) Tlumak, R. L.; Day, J. C.; Slanga, J. P.; Skell, P. S. *J. Am. Chem. Soc.* **1982**, *104*, 7257.

(7) Poutsma, M. L. *J. Am. Chem. Soc.* **1965**, *85*, 2172.

(8) McBain, D. S.; Skell, P. S., to be submitted to the *J. Am. Chem. Soc.*

(9) Bartlett, P. D.; Benzing, E. P.; Pincock, R. E. *J. Am. Chem. Soc.* **1960**, *82*, 1762.

(10) Huyser, E. S. "Free Radical Chain Reactions" Wiley, New York, 1970.

(11) "Landolt-Börnstein", 6th ed. Hausen, H., Ed.; Springer: Berlin, 1976; Vol. IV 4cl.

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

(13) Walling, C.; El-Taliawi, M.; Zhao, C. *J. Am. Chem. Soc.* **1983**, *105*, 5119.

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

addition of pentane. The reaction conditions are listed in Table I; the physical data of the addition products **5a–e** are listed in Table III.

Addition Products 5f–i. The addition products of *N*-bromophthalimide (**1b**) with the different alkenes **3** were prepared as described above. All reactions were carried out under heterogeneous conditions. Upon completion of the irradiation period (Table II) the volatiles were removed by vacuum distillation, and the solid residue was extracted with CCl_4, in which unreacted *N*-bromophthalimide and phthalimide are virtually insoluble. The CCl_4 washes were collected and filtered, and the solvent was removed under vacuum. The residue was taken up in CCl_4 and chilled, and pentane was added until precipitation began. Crystallization was done twice. The physical properties of the addition products **5f–i** are summarized in Table IV.

Competition Procedure. The competition reactions were carried out as in the syntheses with *N*-bromo-3,3-dimethylglutarimide 1a. The solid residue after evaporation of the volatiles under high vacuum was dissolved in $CDCl_3$ and investigated by NMR, with hexamethyldisiloxane as internal standard.

With the *N*-bromophthalimide (**1b**) the solids were extracted with $CDCl_3$, filtered, and the filtrate was investigated by NMR, with hexamethyldisiloxane as internal standard.

Kinetic Experiments. A mixture of 0.20 mmol of 33DMNBG (**1a**), 0.23 mmol of 2-chloropropene (**3d**), 1 mL of CD_2Cl_2, and 100 μL of a 0.085 M TBPO solution in CH_2Cl_2 was degassed in a NMR tube by using a freeze–pump–thaw technique 5 times. The NMR tube was sealed, and the reaction was monitored by NMR at 35 °C for 2.5 h.

A similar experiment with ethylene (**3a**) was carried out by using 0.14 mmol of 33DMNBG (**1a**), 0.4 mmol of ethene (**3a**), 0.9 mL of CD_2Cl_2, and 0.3 μmol of TBPO. The ethyne concentration in solution was determined by NMR.

The results are summarized in Table XI.

Competition between Cyclohexane and Ethene. A mixture of 550 μmol of 33DMNBG (**1a**), 5 mL of CH_2Cl_2, 4.6 mmol of cyclohexane, and 1.51 mmol of ethene (**3a**) were degassed 5 times in a 30-mL Pyrex pressure tube by freeze–pump–thaw cycles. UV irradiation with a 400-W mercury arc at 11 °C through Pyrex at a distance of 5 cm for 9 min led to 140 μmol of addition product **5a** and 370 μmol of bromocyclohexane. The concentration of ethene (**3a**) in solution (0.15 M, 0.84 mmol) was calculated by Henry's law by using solubilities for similar solvents (0.013 mol fraction per bar). The relative rate constant was calculated to be $k(C_6H_{12}/C_2H_4) = 0.55$.

Acknowledgment. This work was carried out with financial support from the National Science Foundation and the PRF fund of the American Chemical Society. U.L. thanks the Alexander von Humboldt Foundation for a partial stipendium from the Lynen Fund.

Registry No. **1a**, 66393-63-3; **1b**, 2439-85-2; **3a**, 74-85-1; **3b**, 108-05-4; **3c**, 557-98-2; **3d**, 115-11-7; **3e**, 558-37-2; **5a**, 101079-07-6; **5b**, 101079-10-1; **5c**, 101079-11-2; **5d**, 101079-09-8; **5e**, 101079-08-7; **5f**, 101079-12-3; **5g**, 101079-13-4; **5h**, 101079-14-5; **5i**, 101079-15-6; $CH_2{=}CCl_2$, 75-35-4; $Cl_2C{=}CCl_2$, 127-18-4; cyclohexane, 110-82-7; benzene, 71-43-2; fumaronitrile, 764-42-1; maleic anhydride, 108-31-6; neopentane, 463-82-1.

Oxidation of Molecules Containing Two Tetraalkylhydrazine Units

Stephen F. Nelsen* and Mark R. Willi

S. M. McElvain Laboratories of Organic Chemistry, Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706

John M. Mellor and Neil M. Smith

Department of Chemistry, The University, Southampton S09 5NH, U.K.

Received September 10, 1985

Cyclic voltammetry studies have been carried out on several bishydrazines. $Me_2NNMe(CH_2)_nNMeNMe_2$, $n = 2$–4 (**2–4**), and 1,4-bis(dimethylamino)piperazine (**11**) have only a small separation between their first and second oxidation potentials and give dications which are short-lived in solution (lifetimes below a few milliseconds). In contrast, pentacyclic bishydrazine **14** and tetracyclic bishydrazines **16** and **17** have formal potentials that differ by 0.29, 0.21, and 0.19 V, respectively, and give dications which are long-lived in solution (their lifetimes exceed seconds). Hexacyclic bishydrazines **12** and **13** have a much larger separation in formal potentials for oxidation and give short-lived dications. The shapes of the tetracyclic and pentacyclic compounds are discussed, as is the implication of these results for the consideration of a hydrazine radical cation interacting with a neutral hydrazine.

Considerable study has established that electron loss from tetraalkylhydrazines (R_4N_2) has most unusual thermodynamic and kinetic features.[1] The relative thermodynamics of electron loss may be conveniently established by cyclic voltammetry (CV) for a wide range of R groups because the oxidized form $R_4N_2^+$ is usually long-lived in the presence of the basic neutral form. The effects of changing R groups are notably large; $R_4N_2,R_4N_2^+$ couples covering a $\Delta G°$ range of 30 kcal/mol are known. This occurs because there is a large difference in preferred geometry for the two oxidation states. Neutral R_4N_2 has a strong preference for pyramidal nitrogen atoms (lone pair hybridization about sp^3) and a weak preference for perpendicular lone pairs (lone pair, lone pair dihedral angle $\theta = 90°$). The oxidized form $R_4N_2^+$ has a strong preference for coplanar lone pair orbitals ($\theta = 180°$ or $0°$) and a weak preference for planar nitrogen atoms (lone pair hybridication about pure p). Geometrical demands of the R groups, especially in cyclic systems, can substantially strain either the reduced or oxidized form, leading to the large effects observed on $\Delta G°$. Electron transfer is also unusually slow for $R_4N_2,R_4N_2^+$ couples. The large change in geometry at the hydrazine nitrogens upon electron transfer results in the electron-transfer transition state being considered distorted from the equilibrium geometry of either

---

[1] (a) Nelsen, S. F. *Acc. Chem. Res.* **1981**, *14*, 131. (b) Nelsen, S. F. "Hydrazine, Hydrazine Cation Electron Transfer Reactions" *Molecular Structures and Energetics*; Liebman, J. F., Greenberg, A., Eds.; VCH: Deerfield Beach, FL, 1986; Vol. 3, Chapter 1, in press.

0022-3263/86/1951-2081$01.50/0 © 1986 American Chemical Society