Absolute Rate Constants for Bromine Abstraction from *N*-Bromoimides and Br_2 by Alkyl Radicals

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Abstract: Imidyl radicals react with cyclopropanes solely via hydrogen abstraction. In the case of methylcyclopropane, the major product (cyclopropylcarbinyl bromide) is derived from abstraction of hydrogen from the methyl group. The resultant cyclopropylcarbinyl radical is partitioned between two pathways: (1) abstraction of Br from *N*-bromoimide and (2) rearrangement to the allylcarbinyl radical (eventually yielding 4-bromo-1-butene). Since the absolute rate of the rearrangement is known, an absolute rate constant for the abstraction of Br from *N*-bromoimides by alkyl radicals can be derived (CH_2Cl_2 solvent, 15 °C), $k \approx (1.3\text{-}1.6) \times 10^{10}$ M^{-1} s^{-1}. Reactions carried out in the presence of Br_2 provide a *third* pathway for scavenging of the cyclopropylcarbinyl radical, providing $k_{Br_2} = 2.2 \times 10^{10}$ M^{-1} s^{-1}. Thus, trapping of primary R• by *either* *N*-bromoimides or Br_2 occurs at rates that are diffusion-controlled.

I. Introduction

Despite the importance of halogen atom transfer from molecular halogen (X_2) or *N*-bromoimides (NX) to alkyl radicals as the final chain-propagating link in many halogenation reactions, little information is available regarding the *rate* of these reactions. Utilization of the cyclopropylcarbinyl–allylcarbinyl free radical "clock"[1] for reactions of primary alkyl radical has made these values accessible.

In a free radical chain process, the highly reactive imidyl radical abstracts hydrogen from methylcyclopropane (MCP) to make a cyclopropylcarbinyl radical. In competition with bromine abstraction from *N*-bromoimide, cyclopropylcarbinyl radical rearranges to the butenyl radical, $CH_2{=}CHCH_2CH_2^{\bullet}$, with a well-established rate constant.[2] Bimolecular rate constants for trapping by various halogen atom donors, *N*-bromo-3,3-dimethylglutarimide (NBG), *N*-bromophthalimide (NBP), or Br_2, were determined from the relative yields of rearranged and unrearranged products as a function of concentration of the trapping agent.

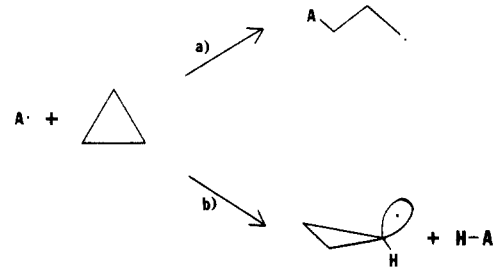
II. Results

A. Reactions of Radicals with Cyclopropanes. The products of the reaction between a free radical and cyclopropane are strongly dependent on the identity and nature of the attacking radical (A•). Generally, two pathways are important (Scheme I): ring opening (path a) and hydrogen abstraction (path b). For Br•, ring opening is the only important reaction pathway,[3] while for Cl• both ring opening and hydrogen abstraction are important processes.[4] For *tert*-butoxy[4] and succinimidyl[5] radicals, hydrogen abstraction is the only significant process.

B. Reaction of Methylcyclopropane (MCP) with Br_2. At −78 °C, the photoinitiated reaction of cyclopropane with Br_2 is reported to yield *only* 1,3-dibromopropane. Similarly, reaction with MCP results in exclusive formation of 1,3-dibromobutane. In neither instance are products derived from hydrogen abstraction observed.[3] We confirm these observations at −78 °C and further extend them to the temperatures at which we run our *N*-bromoimide reactions (10–20 °C).

Solutions containing Br_2 (0.98 mmol) and MCP (7.1–7.4 mmol) in 5.0 mL of CCl_4 were prepared. After 66 h at 14 °C in the dark, only 0.296 mmol (30%) of the Br_2 was consumed ($CH_2{=}CH_2$ was added, and Br_2 determined by GLC as dibromoethane). In contrast, when illuminated in the absence of O_2, Br_2 color was completely discharged in less than 30 min. The sole reaction product was 1,3-dibromobutane; no other products were observed.

Scheme I



C. Reaction of Cyclopropane with 3,3-Dimethyl-*N*-bromoglutarimide (NBG). Procedures for observing imidyl radical (N•) chains in reactions of *N*-bromoimides (NBr) have been extensively discussed in the literature[6] and involve taking precautions that limit (or exclude) competing chains based on bromine atom. In our laboratory, two procedures have proven particularly successful: (1) utilization of solvents that permit large concentrations of *N*-bromoimide to be employed (e.g., CH_2Cl_2, CH_3CN), thereby *increasing* the rate of the imidyl chain propagating step, $R^{\bullet} + NBr \rightarrow RBr + N^{\bullet}$, and (2) including alkenes to scavenge Br_2, thus, *decreasing* the rate of the bromine chain propagating step, $R^{\bullet} + Br_2 \rightarrow RBr + Br^{\bullet}$.

Traynham and Lee found that the cyclopropane-derived products obtained from reaction of *N*-bromosuccinimide (NBS) with cyclopropane in acetonitrile contained >98% cyclopropyl bromide and <2% 1,3-dibromopropane. The disparity between this reaction and the analogous reaction of Br_2 (100% yield 1,3-dibromopropane) was given as evidence for succinimidyl radical intermediacy.[5]

Thus, the use of cyclopropanes as substrates provides a *third* method for observing imidyl behavior since (1) cyclopropanes are good bromine atom scavengers, forming easily recognized products (1,3-dibromides), and (2) substitution products (monobromides) arise *solely* from hydrogen abstraction by imidyl radical.

Reaction of NBG with cyclopropane gave results analogous to the NBS reaction, with the advantage that glutarimidyl radical does not undergo the ring-opening reaction which is the dominant reaction for succinimidyl. A photoinitiated reaction of NBG (0.492 mmol) with cyclopropane (7.52 mmol) in CH_2Cl_2 (5.0 mL, 78.0 mmol) yielded cyclopropyl bromide (0.259 mmol, 53%), $CHBrCl_2$ (0.204 mmol, 42%), and a trace amount of 1,3-dibromopropane as the only Br-containing products.

(1) For an excellent review on the utilization of free radical clocks, see: Griller, D.; Ingold, K. U. *Acc. Chem. Res.* **1980**, *13*, 317.
(2) Mathew, L.; Warkentin, J. *J. Am. Chem. Soc.* **1986**, *108*, 7981. For earlier evaluations, see also: Maillard, B.; Forrest, D.; Ingold, K. U. *J. Am. Chem. Soc.* **1976**, *98*, 7024. Effio, A.; Griller, D.; Ingold, K. U.; Beckwith, A. L. J.; Serelis, A. K. *J. Am. Chem. Soc.* **1980**, *102*, 1734.
(3) Shea, K. J.; Skell, P. S. *J. Am. Chem. Soc.* **1973**, *95*, 6728.
(4) Walling, C.; Fredricks, P. S. *J. Am. Chem. Soc.* **1962**, *84*, 3326.
(5) Traynham, J. C.; Lee, Y.-S. *J. Am. Chem. Soc.* **1974**, *96*, 3590.
(6) For a recent review, see: Lüning, U.; Skell, P. S. *Tetrahedron* **1985**, *41*, 4289.

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Table I. Photoinitiated[a] Reaction of *N*-Bromo-3,3-dimethylglutarimide with Methylcyclopropane

product	% yield[b]	% yield[b,c]
$CHBrCl_2$	24.1	12.8
$CH_2{=}CHCH_2CH_2Br$	3.2	1.7
$c\text{-}C_3H_5CH_2Br$	34.5	18.0
1,3-dibromobutane	8.5	trace
3 C_4H_7Br isomers	18.2	9.0
GH[d]	95.9	50.4
GCH_2CH_2Br[d]		50.1
1,2-dibromoethane		2.0

[a] Irradiated with a 400-W medium-pressure Hg arc lamp through Pyrex for 1 h at 15 °C. [b] 0.1 M *N*-bromo-3,3-dimethylglutarimide and 1.3 M methylcyclopropane in CH_2Cl_2. [c] 0.1 M $CH_2{=}CH_2$ present. [d] G = 3,3-dimethylglutarimidyl.

Scheme II

$$c\text{-}C_3H_5\text{-}CH_3 + G^\bullet \longrightarrow c\text{-}C_3H_5\text{-}CH_2^\bullet + GH$$

$$c\text{-}C_3H_5\text{-}CH_2^\bullet \xrightleftharpoons{k_0} CH_2{=}CHCH_2CH_2^\bullet$$

$$c\text{-}C_3H_5\text{-}CH_2^\bullet + NBG \xrightarrow{k_{NBG}} c\text{-}C_3H_5\text{-}CH_2Br + G^\bullet$$

$$CH_2{=}CHCH_2CH_2^\bullet + NBG \longrightarrow CH_2{=}CHCH_2CH_2Br + G^\bullet$$

In the presence of 0.044 M $CH_2{=}CH_2$ (NBG, 0.464 mmol; $c\text{-}C_3H_6$, 3.64 mmol; CH_2Cl_2, 5.0 mL, 78.0 mmol), the observed products were cyclopropyl bromide (0.102 mmol, 22%), $CHBrCl_2$ (0.110 mmol, 24%), and *N*-(2-bromoethyl)-3,3-dimethylglutarimide (NBG/$CH_2{=}CH_2$ adduct, 0.185 mmol, 40%). 3,3-Dimethylglutarimide (GH), the companion product of hydrogen abstraction, was also formed (0.209 mmol, 45%).

This data permits the rate of hydrogen abstraction from $c\text{-}C_3H_6$ relative to addition to $CH_2{=}CH_2$ to be calculated for G•, $k(c\text{-}C_3H_6)/k(CH_2{=}CH_2) = 0.0067$ (per molecule basis). From this value, and other published selectivity data for G•, the following reactivity order can be calculated (per hydrogen basis): secondary H (6–7) > primary H (1.00) > $c\text{-}C_3H_6$ (C–H) (0.31). The decreased reactivity of a cyclopropyl C–H bond has also been observed for other free radicals (e.g., C• and *t*-BuO•)[4] and can be attributed to the high C–H bond dissociation energy of cyclopropane: 106 kcal/mol[7] compared to 100 kcal/mol for a 1° C–H bond.[8]

D. Reaction of Methylcyclopropane (MCP) with *N*-Bromo-3,3-dimethylglutarimide (NBG). 1. Products and Mechanism. Product yields and reaction conditions for the reaction of NBG with MCP (in CH_2Cl_2) are given in Table I. The predominant MCP-derived product was cyclopropylcarbinyl bromide, arising from abstraction of a methyl hydrogen. 4-Bromo-1-butene arises via the cyclopropylcarbinyl–allylcarbinyl rearrangement (eq 1).

$$c\text{-}C_3H_5\text{–}CH_2^\bullet \rightarrow CH_2{=}CHCH_2CH_2^\bullet \qquad (1)$$

No 1,2,4-tribromobutane, potentially resulting from the addition of Br_2 to 4-bromo-1-butene, was detected. Additionally, three other products, formed in a 4.4:2.3:1 ratio and identified by GCMS as C_4H_7Br isomers, can be assigned to the three possible products that would arise from hydrogen abstraction from the cyclopropane ring of MCP: 1-bromo-1-methylcyclopropane, *cis*- and *trans*-1-bromo-2-methylcyclopropane.

The 3,3-dimethylglutarimidyl radical (G•) is the *only* hydrogen abstractor operating in this system since the alternate potential chain carrier, Br•, reacts via an S_H2 process yielding 1,3-dibromobutane.[3] Since Br• is produced in the photoinitiation step, the chain lengths can be estimated from the ratio of the products from G• reactions (C_4H_7Br's) to those from Br• reactions (1,3-dibromobutane): 8.9 in the absence of C_2H_4, 46 in the presence of C_2H_4.

Scheme II summarizes the reaction of G• with the methyl group of MCP and the ensuing reactions in the chain sequence.

The presence of ethylene in the reaction mixture diverts approximately 50% of G• to the GBr/$CH_2{=}CH_2$ adduct; however, the relative yields of the different hydrogen abstraction products are unperturbed. Thus, with MCP as substrate, utilization of an alkene to suppress Br• chains is unnecessary since MCP serves as Br• scavenger; *the products arising from the G• and Br• reactions are completely different.*

Our primary interest in MCP as a substrate involves clocking the rate of Br abstraction by the 1° cyclopropylcarbinyl radical from NBG, against the cyclopropylcarbinyl–allylcarbinyl rearrangement. Since the absolute rate constant for the rearrangement (k_0) is known,[2] it should be possible to determine the absolute rate of Br abstraction from NBG (k_{NBG}) by studying the product ratio cyclopropylcarbinyl bromide (BrMCP)/4-bromo-1-butene (4-BrBu) as a function of [NBG] (eq 2).

$$(\text{yield of BrMCP})/(\text{yield of 4-BrBu}) = k_{NBG}[NBG]/k_0 \qquad (2)$$

The relatively low yield of 4-bromo-1-butene at 0.1 M NBG indicates k_{NBG} is large relative to k_0. However, a potential complication is that 4-bromo-1-butene may not be stable under the reaction conditions. Previous studies from this laboratory have shown that addition of an imidyl radical to an olefin is a very facile process. For example, addition of G• to *tert*-butylethylene is favored by a factor of 100 over abstraction of a primary hydrogen.[9] Thus, the possible distortion of our results by further reaction of 4-bromo-1-butene with NBG must be considered.

To test this hypothesis, the photoinitiated reaction of NBG with 4-bromo-1-butene in CH_2Cl_2 was studied. As anticipated, the major product was the NBG/alkene addition product, $GCH_2CH(Br)CH_2CH_2Br$ (69%). Other products include 3,3-dimethylglutarimide (30%), $CHBrCl_2$ (12%), and 1,2,4-tribromobutane (3%). Some products of hydrogen abstraction (predominantly 1,4-dibromobut-2-ene) were also detected.

Presence of the NBG/4-bromo-1-butene adduct is readily recognizable by ^1H NMR analysis. In our MCP/NBG reactions, *none* of this product could be detected (detection limit ≤ 5%). Thus, in these experiments, the 4-bromo-1-butene yield is not distorted to any appreciable extent by further reaction with NBG.

Additional support for our contention that little (if any) 4-bromo-1-butene is consumed during the MCP/NBG reaction can be derived from the data in Table I. Addition of an olefin (C_2H_4) has no effect on the BrMCP/4-BrBu ratio: 10.8 in the absence of ethylene, 10.6 in the presence of 1 equiv of ethylene, despite the fact that under the latter conditions, a 50% yield of the NBG/$CH_2{=}CH_2$ addition product results. Thus, these observations rule out the possibility that our product ratios are significantly distorted by secondary reactions of 4-bromo-1-butene under the reaction conditions.

Qualitatively, the amount of 4-bromo-1-butene consumed by NBG during the course of the MCP/NBG reaction could be minimized by running the reaction to low percent conversion. In order to determine the upper limit for the amount of 4-bromo-1-butene consumed under the conditions of our MCP/NBG reactions, some information regarding the relative reactivity of 4-BrBu and MCP toward G• was needed. This information was obtained by direct competitions with neopentane. Since the reaction was followed by 4-BrBu disappearance, the reported reactivity accounts for all possible NBG/4-BrBu reactions. The results of these experiments appear in Table II. As expected, 4-bromo-1-butene is more reactive (32 times) than MCP. Additionally, the methyl hydrogens of MCP are more reactive (3.5 times on a per hydrogen basis) than those of neopentane.

Since 4-BrBu is 32 times more reactive toward G• than MCP, if in our MCP/NBG reactions a ≥10:1 ratio MCP/NBG is employed, the reaction runs to ≤5% NBG conversion, and if one further assumes that 4-BrBu is the sole product of the reaction between MCP and NBG, an insignificant amount (less than 10%) of the 4-bromo-1-butene formed during the course of the reaction would be lost due to further reaction with NBG. Since cyclopropylcarbinyl bromide and *not* 4-bromo-1-butene is the major

(7) McMillen, D. F.; Golden, D. M. *Annu. Rev. Phys. Chem.* **1982**, *33*, 493.
(8) Castelhano, A. L.; Griller, D. *J. Am. Chem. Soc.* **1982**, *104*, 3655.
(9) Lüning, U.; McBain, D. S.; Skell, P. S. *J. Org. Chem.* **1986**, *51*, 2077.

Table II. Relative Reactivities of Methylcyclopropane (MCP) and 4-Bromo-1-butene (4-BrBu) toward the 3,3-Dimethylglutarimidyl Radical (G•)

	4-BrBu vs Me_4C	MCP vs Me_4C
initially[a] (mmol)	NBG (0.519) Me_4C (5.86) 4-BrBu (0.493)	NBG (1.00) Me_4C (1.30) MCP (1.38)
after irradiation[b] (mmol)	4-BrBu (0.277) $(CH_3)_3CCH_2Br$ (0.0801)	C_4H_7Br's (0.048) c-C_3H_5CH2Br + 4-BrBu (0.102) $(CH_3)_3CCH_2Br$ (0.110)
relative rate constant (molecular base) per hydrogen selectivity[c]	k(4-BrBu)/k(Me_4C) = 41	k(MCP)/k(Me_4C) = 1.3 r(c-$C_3H_5CH_3$/Me_4C)$_H$ = 3.5

[a] Five milliliters of CH_2Cl_2; T = 15 °C, irradiated with a 400-W medium-pressure Hg arc lamp (through Pyrex) for 1 h. [b] Only pertinent products are listed. Mass balance ≥ 95%. [c] Per hydrogen selectivity: methyl CH of MCP vs CH of neopentane.

Table III. Ratio of Products Formed in the Photoinitiated Reaction of Methylcyclopropane with *N*-Bromo-3,3-dimethylglutarimide (NBG) at 15 °C

$[NBG]_{init}$,[a] M	yield of BrMCP/yield of 4-BrBu[b]	$[NBG]_{init}$,[a] M	yield of BrMCP/yield of 4-BrBu[b]
0.014	0.87	0.104	13.2
0.051	5.82	0.152	16.4
0.086	7.00	0.215	20.2

[a] $[MCP]_{init} \geq 10[NBG]_{init}$, CH_2Cl_2 solvent; irradiated with a 400-W medium-pressure Hg arc lamp through Pyrex for 3 min; reactions run to ≤5% NBG conversion. [b] BrMCP = cyclopropylcarbinyl bromide; 4-BrBu = 4-bromo-1-butene.

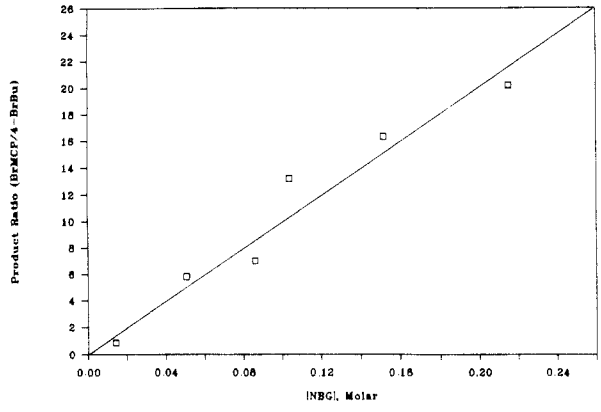


Figure 1. Reaction of *N*-bromo-3,3-dimethylglutarimide (NBG) with methylcyclopropane (MCP). Product ratio (cyclopropylcarbinyl bromide/4-bromo-1-butene) as a function of [NBG].

product of the MCP/NBG reaction, the amount of 4-bromo-1-butene actually lost is insignificant.

2. Absolute Rate Constant for Abstraction of Br from NBG by a Primary Radical. In order to minimize further reaction of 4-bromo-1-butene, two precautions were followed: (1) a large initial [methylcyclopropane]/[NBG] was employed and (2) the reactions were run to low percent conversion (≤5%). The data summarized in Table III were obtained at various initial concentrations of NBG. The product ratio BrMCP/4-BrBu increases linearly with increasing NBG concentration (Figure 1). Analysis of the data according to eq 2 yields k_{NBG}/k_0 = 100 (±5) M^{-1}. Since at 15 °C, $k_0 = 1.3 \times 10^8$ s^{-1},[2] $k_{NBG} = 1.3 \times 10^{10}$ M^{-1} s^{-1}.

E. Reaction of Methylcyclopropane with *N*-Bromophthalimide (NPB). Absolute Rate Constant for Abstraction of Br from NBP by a Primary Radical. The products of the photoinitiated reaction of NBP with MCP are the same as with the analogous NBG reaction: Photolysis of 0.10 M NBP, 1.8 M MCP in CH_2Cl_2 (homogeneous mixture) yielded $CHBrCl_2$ (5.3%), three C_4H_7Br isomers in a ratio of 6.9:2.4:1 (18.6%), 4-bromo-1-butene (2.3%), cyclopropylcarbinyl bromide (36%), and 1,3-dibromobutane (16.3%). 1,3-Dibromobutane, formed by reaction of Br• with methylcyclopropane, is the only product formed via ring opening of the cyclopropane ring. Clearly, phthalimidyl radical (P•) is the hydrogen abstractor in this system, and a mechanism analogous to Scheme II is operating. The distribution of the C_4H_7Br isomers is somewhat different from the NBG reaction, explicable by P• vs G• as chain carrier. As with NBG, the product ratio BrMCP/4-BrBu was studied as a function of [NBP] at high [MCP]/[NBP], low (<5%) NBP conversion (Table IV, Figure 2). Application of eq 2 yields k_{NBP}/k_0 = 120 (±10) M^{-1}; k_{NBP} = 1.6×10^{10} M^{-1} s^{-1} (15 °C).

Table IV. Ratio of Products Formed in the Photoinitiated Reaction of Methylcyclopropane (MCP) with *N*-Bromophthalimide (NBP) at 15 °C

$[NBP]_{init}$,[a] M	yield of BrMCP/yield of 4-BrBu[b]	$[NBP]_{init}$,[a] M	yield of BrMCP/yield of 4-BrBu[b]
0.022	4.08	0.083	11.7
0.045	6.95	0.139	14.4

[a] $[MCP]_{init} \geq 10[NBP]_{init}$, CH_2Cl_2 solvent; irradiated with a 400-W medium-pressure Hg arc lamp through Pyrex for 3 min; reactions run to ≤5% NBP conversion. [b] BrMCP = cyclopropylcarbinyl bromide; 4-BrBu = 4-bromo-1-butene.

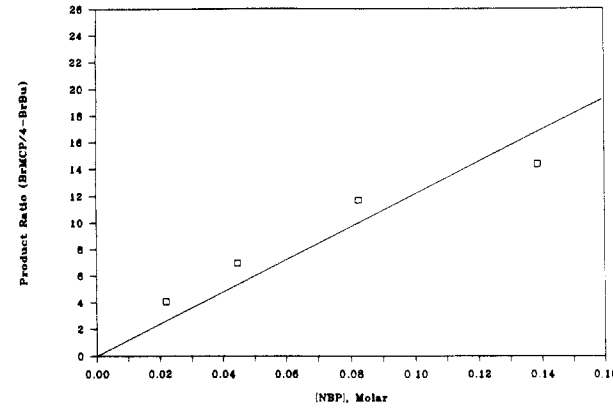


Figure 2. Reaction of *N*-bromophthalimide (NBP) with methylcyclopropane (MCP). Product ratio (cyclopropylcarbinyl bromide/4-bromo-1-butene) as a function of [NBP].

F. Effect of Added Br_2 on the NBG/Methylcyclopropane Reaction. Since reaction of Br_2 with cyclopropanes yields only 1,3-dibromides,[3] it is not possible to determine the rate of reaction of cyclopropylcarbinyl radical with Br_2 with the MCP/Br_2 reaction. However, it is possible to obtain this information by photobromination of MCP by NBG in the *presence* of Br_2.

Evidence has been presented that suggests the existence of a third hydrogen abstractor (besides Br• or imidyl) in *N*-bromoimide/Br_2 systems, but its identity is unclear.[10] However, this is not important for our purposes since the chemistry of interest, cyclopropylcarbinyl ring opening vs Br abstraction, occurs *after* hydrogen abstraction.

With one exception, the products of reaction between NBG and MCP are the same in the presence or absence of Br_2. The *exception* is that in the presence of Br_2, 1,2,4-tribromobutane is also formed, arising from the subsequent addition of Br_2 to the 4-bromo-1-butene. Although Br_2 is rapidly depleted during the course of the reaction forming 1,3-dibromobutane, formation of

(10) Skell, P. S.; Lüning, U.; McBain, D. S.; Tanko, J. M. *J. Am. Chem. Soc.* **1986**, *108*, 121.

Table V. Ratio of Products Formed in the Photoinitiated Reaction of Methylcyclopropane (MCP) with *N*-Bromo-3,3-dimethylglutarimide (NBG) in the Presence of Varying Concentrations of Bromine

[NBG],[a] M	$[Br_2]$, M	PR[b]	PR'[c]
0.196	0.098	30.3	10.4
0.147	0.128	42.5	27.7
0.209	0.200	54.2	33.1
0.201	0.420	94.1	73.8

[a] $[MCP]_{init} \geq 10[NBG]_{init}$, $10[Br_2]_{init}$, CCl_4 solvent; irradiated with a 75-W tungsten lamp through Pyrex for 3 min; reactions run to low percent Br_2 conversion. [b] PR = yield cyclopropylcarbinyl bromide/yield 1,2,4-tribromobutane. [c] "Corrected" product ratio, PR − k_{NBG}·[NBG]/k_0; see text.

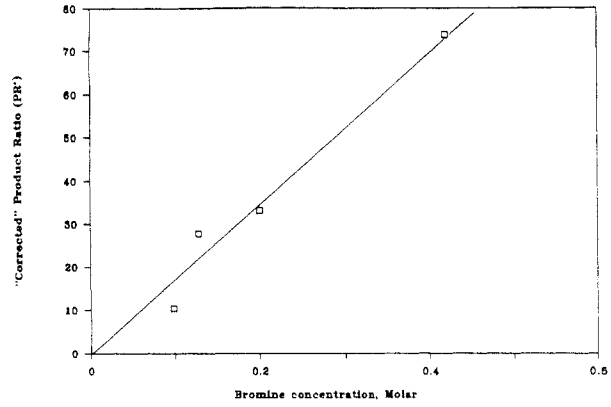


Figure 3. Reaction of *N*-bromo-3,3-dimethylglutarimide (NBG) with methylcyclopropane (MCP) in the presence of Br_2. Product ratio (bromomethylcyclopropane/1,2,4-tribromobutane, corrected; see text) as a function of $[Br_2]$.

the tribromide indicates that hydrogen abstraction by imidyl occurs before all the Br_2 is depleted. If the opposite were true (i.e., the NBG/MCP reaction occurred after depletion of Br_2), no tribromide would be formed at all. Consequently, some portion of the cyclopropylcarbinyl bromide must be formed by reaction of R• with Br_2, as well as R• + NBG. The enhancement of the product ratio (BrMCP/ring-opened product) observed when Br_2 is present confirms this hypothesis (vide infra).

In this system, cyclopropylcarbinyl radical partitions itself between three reaction pathways, k_0, k_{NBG}, and k_{Br_2}. Bunnett has labeled this type of competition as "ad eundum fructus" meaning "to the same product".[11] Equation 3 describes the product ratio, PR = BrMCP/tribromide, as a function of [NBG] and $[Br_2]$.

$$PR = (k_{Br_2}/k_0)[Br_2] + (k_{NBG}/k_0)[NBG] \quad (3)$$

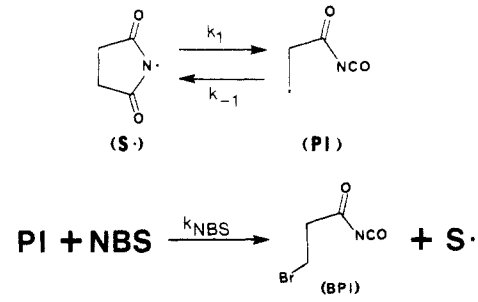
Table V summarizes the results obtained when MCP was allowed to react with NBG in the presence of varying $[Br_2]$. These reactions were carried out to low percent Br_2 conversions so as to keep $[Br_2]$ approximately constant. In each instance, *the product ratio is substantially higher than would be expected if cyclopropylcarbinyl radical were reacting solely with NBG.*

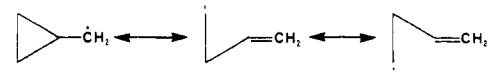
Since [NBG] is held constant, the values of $[k_{NBG}[NBG]/k_0]$ can be subtracted from PR to give PR', which when plotted against $[Br_2]$ (Figure 3) yields a straight line whose slope is equal to k_{Br_2}/k_0. Thus, the rate constant ratio $k_{Br_2}/k_0 = 170\ (\pm 14)\ M^{-1}$ is derived from this treatment; $k_{Br_2} = 2.2 \times 10^{10}\ M^{-1}\ s^{-1}$ (15 °C).

III. Discussion

Imidyl radicals react with cyclopropanes solely via hydrogen abstraction. For methylcyclopropane (MCP), hydrogen abstraction occurs also at the methyl group. Our results indicate a methyl hydrogen of MCP is 3.5 times as reactive as a primary hydrogen of neopentane. Enhanced reactivity of the methyl hydrogens has also been reported for Cl• and *t*-BuO•[4] and can be attributed to hyperconjugative stabilization of the cyclopropylcarbinyl radical (eq 4).

Scheme III





(4)

Absolute rate constants for reaction of molecular halogens (X_2) or *N*-haloimides with alkyl radicals have been generally unavailable, particularly for X = Br, although it is often assumed the reaction between alkyl radicals and Br_2 is diffusion-controlled. (The gas phase reaction CH_3• + Br_2 → CH_3Br + Br• is 25.5 kcal/mol exothermic.)[12]

The rate of reaction between R• and NBS has been stated to be ca. 1000 times slower than the Br_2 reaction. This conclusion was based on the *qualitative* observation of the loss of optical activity of the 1,2-dibromo-2-methylbutane, formed in the photobromination of (+)-1-bromo-2-methylbutane: Br_2 was >1000 times more efficient in trapping the chiral intermediate.[13] However, the radical in these experiments was a tertiary bridged-bromine radical, whose reactivity was apparently much less than a primary alkyl radical. It is reasonable to expect less reactive radicals to show a larger difference for k_{Br_2}/k_{NBS}.

The results presented here suggest that trapping of 1° alkyl radicals by Br_2, *N*-bromo-3,3-dimethylglutarimide (NBG), and *N*-bromophthalimide (NBP) are essentially diffusion-controlled, having rate constants 2.2×10^{10}, 1.3×10^{10}, and $1.6 \times 10^{10}\ M^{-1}\ s^{-1}$, respectively. The calculated diffusional rate constant in CH_2Cl_2 at 15 °C (calculated from $k_{diff} = 8RT/3000\eta$, $\eta(CH_2Cl_2$, 15 °C) = 0.449 cp)[14] is $1.4 \times 10^{10}\ M^{-1}\ s^{-1}$. Further, since the structure of the imidyl fragment appears to have little effect on the rate constant, we suggest provisionally that this value is general for *N*-bromoimides. The usual statistical factors taking account of the number of reactive sites are applicable in slower reactions, but are not relevant for reactions in which the intrinsic rate exceeds the rate of cage escape, as in the cases of encounter-controlled rates. Thus, the somewhat larger rate constant for Br_2 must be largely attributed to other factors.

Extension of this experimental procedure should enable absolute rates of trapping of alkyl radicals by Cl_2, *t*-BuOCl, BrCl, *N*-chloroimides, etc. to be determined and will be the topic of future investigations in this laboratory. Rough estimates of some of these rates can be made from data already in the literature.

The rate of reaction between R• + Cl_2 is estimated to be $2.3 \times 10^9\ M^{-1}\ s^{-1}$ (gas phase).[15] On the basis of laser flash photolysis results, Ingold et al. have estimated that in solution the rate constant is $\gg 10^7\ M^{-1}\ s^{-1}$.[16] In 1962, Walling reported that photochlorination of MCP ($[Cl_2]_{init} \sim 3.2$ M) yielded >50% cyclopropylcarbinyl chloride.[4] No 4-chloro-1-butene was observed,

(11) Bunnett, J. F. *Techniques of Chemistry*; Lewis, E. S., Ed.; Wiley-Interscience: New York, 1974; Vol. VI, Part 1, pp 161–165.

(12) Heats of formation of all pertinant species taken from: Benson, S. W. *Thermochemical Kinetics*, 2nd ed.; Wiley: New York, 1976.

(13) Skell, P. S.; Tuleen, D. L.; Readio, P. D. *J. Am. Chem. Soc.* **1963**, *85*, 2805.

(14) *Handbook of Chemistry and Physics*, 53rd ed.; Weast, R. C., Ed.; CRC: Cleveland, 1972.

(15) Kerr, J. A. In *Free Radicals*, Kochi, J. K., Ed.; Wiley: New York, 1973; Vol. 1.

(16) Bunce, N. J.; Ingold, K. U.; Landers, J. P.; Lustyk, J.; Scaiano, J. C. *J. Am. Chem. Soc.* **1985**, *107*, 5464.

and only a trace amount of 1,2,4-trichlorobutane was detected, suggesting to us that the c-$C_3H_7CH_2^{\bullet}/Cl_2$ reaction must also be diffusion-controlled.

The results we have presented also allow us to correct some of our earlier interpretations, specifically that k_{NBS} was ca. 20 times smaller than we find here. The free-radical isomerization of NBS to β-bromopropionyl isocyanate (BPI) is interpreted according to Scheme III.[17]

We previously determined k_{-1}/k_{NBS} to be 0.035 M.[17] Assuming k_{NBS} and k_{NBG} are equal, the rate of ring closure of the primary alkyl radical PI to S$^{\bullet}$ is calculable; $k_{-1} = 5 \times 10^8$ s^{-1}. Further, since trapping of PI by *N*-chlorosuccinimide (NCS) is at least 50 times less efficient than NBS,[17] $k_{NCS} \leq 2.6 \times 10^8$ M^{-1} s^{-1}.

It should be noted that this reevaluation of k_{-1}, and the original work on which it is based, is clearly separated from the controversy concerning the involvement of π and σ radicals. The earlier estimate of k_{-1} was based (p 7262, column 2 of ref 17) on two assumptions: (1) $k_1 = k_{-1}$, and (2) the concentration of Br_2 required to quench formation of BPI was $\simeq 10^{-3}$ M. With the new information, it is no longer necessary to use these approximations, which are now recognized to be incorrect by a factor of 10–15.

IV. Experimental Section

General Considerations. ^{1}H NMR spectra were recorded on either a Varian EM-360 (60 MHz) or a Bruker WH-200 (200 MHz) spectrometer, with chemical shifts reported on the δ scale relative to hexamethyldisiloxane (δ = 0.07). Mass spectra were taken on a Kratos 9/50 instrument at 70 eV. Gas chromatographic analyses were carried out on either a Hewlett-Packard HP 5790A or HP 5890 instrument, each equipped with a DB-5 capillary column (30 m × 0.25 mm), FID detector, and an HP 3390A reporting integrator.

Materials. Methylcyclopropane (ICN), as received, contained a significant amount of olefin impurity (butenes?), which were removed by treatment with excess Br_2. Unreacted Br_2 was quenched with corn oil (Mazola). MCP was distilled through two −78 °C traps and collected at −196 °C. By this procedure, MCP of purity ≫99% (GLC) was obtained. Neopentane (Matheson, research grade, 99.6%) was purified as described previously.[10] The following were used as received: bromine (Aldrich), chlorobenzene (Aldrich, HPLC grade), dichloromethane (Aldrich, anhydrous, gold label, 99+%), ethene (Matheson, research grade, 99.99+%), hexamethyldisiloxane (Aldrich), and tetrachloromethane (Fischer). The preparations of *N*-bromo-3,3-dimethylglutarimide (NBG)[9] and *N*-bromophthalimide (NBP)[18] have been described previously.

Authentic samples of the following were commercially available: 4-bromo-1-butene (Aldrich), bromodichloromethane (Pfaltz and Bauer), cyclopropylcarbinyl bromide (Aldrich), 1,3-dibromobutane (Aldrich), 1,2-dibromomethane (Aldrich), 1,3-dibromopropane (Aldrich), and neopentyl bromide (Pfaltz and Bauer). 1,2,4-Tribromobutane was prepared by the addition of Br_2 to 4-bromo-1-butene.

Preparation of *N*-(2,4-Dibromobutyl)-3,3-dimethylglutarimide. NBG (0.181 g, 0.823 mmol), 5.0 mL of CH_2Cl_2, and 0.10 mL of 4-bromo-1-butene (0.985 mmol) were combined in a 30-mL pressure tube, degassed 3 times (freeze–pump–thaw method), and irradiated for 70 min with a 400-W medium-pressure mercury arc lamp (through two Pyrex layers). Afterward, the volatile materials were removed by a high-vacuum trap-to-trap distillation (room temperature). The resulting solid (which by ^{1}H NMR analysis vs hexamethyldisiloxane was shown to contain 0.571 mmol of GBr/4-BrBu adduct, 0.334 mmol of GH), was dissolved in CH_2Cl_2, washed successively with 5% NaOH and H_2O, dried over $MgSO_4$, and evaporated. Passage through a short silica gel column yielded pure GBr/4-BrBu adduct. ^{1}H NMR (60 MHz): δ 1.06 (s, 6 H), 2.20 (m, 2 H), 2.49 (s, 4 H), 3.44 (t, J = 5.0 Hz, 2 H) 3.75–4.5 (m, 3 H). IR (CCl_4): 2990 (m), 2950 (m), 2880 (m), 1740 (m), 1690 (s) cm^{-1}. CI-MS (relative intensity): *m/e* 276 (51.4), 274 (51.9) (M − Br), 194 (9.9), 154 (13.5), 142 (38.6), 86 (50.9), 85 (23.3), 84 (80.6), 49 (100).

Competition Experiments. General Procedure. Reagents (except Br_2) were combined in a 30-mL pressure tube (sealed with an O-ringed Teflon needle valve) and degassed with the freeze–pump–thaw technique (3–5 times). Br_2 (if added), was degassed on the vac-line and distilled directly into the reaction mixture. The mixture was irradiated (through two Pyrex layers) with either a 400-W medium-pressure Hg arc or 75-W tungsten lamp. Reaction times and temperatures are given in the tables and/or text. For reactions in the presence of bromine, excess Br_2 was quenched with ethylene. Volatiles and nonvolatiles were separated by a room temperature high-vacuum trap-to-trap distillation. The volatiles (mono-, di-, and tribromides) were analyzed by GLC (vs PhCl, utilizing a predetermined correction factor). Retention times of products were compared to that of an authentic sample. The nonvolatiles (e.g., GBr, GH, GBr/alkene adduct, etc.) were analyzed by ^{1}H NMR (60 or 200 MHz, depending on the complexity of the signal) vs hexamethyldisiloxane as an internal standard. Unreacted NBP was quantitated iodometrically.

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

(18) Day, J. C.; Govindaraj, N.; McBain, D. S.; Skell, P. S.; Tanko, J. M. *J. Org. Chem.* **1986**, *51*, 4959.