

## Conformational Effects in Free-Radical Hydrogen Abstraction from Medium-Ring Cycloalkanes<sup>1</sup>

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Received January 28, 1974

The ease of free-radical hydrogen abstraction from cycloalkanes containing from 5 to 12 carbon atoms is compared with the reactivity of open-chain methylene groups. Activation energies for abstraction from open-chain positions are generally larger than those for all the cycloalkanes studied except cyclohexane. The results are discussed in terms of the release or aggravation of conformational strain upon forming the  $sp^2$  radical center and, for the  $C_8$ - $C_{12}$  compounds, of the inaccessibility of the C-H bonds toward attack. A recent proposal that the relative ease of forming primary, secondary, and tertiary free radicals is predominantly steric in origin is discussed.

The effect of ring size on the reactivity of cycloalkyl compounds has been extensively studied for ionic reactions, the variations in rate within a reaction series being ascribed to the aggravation or release of conformational strain upon rehybridization of the reactive center at the transition state.<sup>3-5</sup> In contrast, very few similar studies of reactions proceeding through free radical intermediates have been made. Overberger, *et al.*, investigated the decomposition of azobis(cycloalkanecarbonitriles);<sup>6</sup> Rüchardt and his associates decomposed related azocycloalkanes<sup>7</sup> and *tert*-butyl cycloalkanecarboxylic peresters<sup>8</sup> with a view to establishing the stability order of cycloalkyl free radicals.

A problem with these studies is that the mechanism of neither reaction is entirely unambiguous, whereas if relative rates of decomposition are to provide information about radical stability, it is imperative that the radical concerned be shown unequivocally to form in the rate-limiting step of the decomposition. In the case of *tert*-butyl perester decompositions, two extreme mechanisms, involving one-bond ( $RCO_2-OC_4H_9$ ) and two-bond ( $R-CO_2-OC_4H_9$ ) fission, have been distinguished; Bartlett and his colleagues<sup>9</sup> have classified them on the basis of activation parameters. Unfortunately, most of the  $R =$  cycloalkyl examples fall near the boundary between the two classes. Likewise, aliphatic azo compounds were all thought<sup>10</sup> to decompose by simultaneous two-bond cleavage ( $R-N=N-R \rightarrow 2R\cdot + N_2$ ); recent evidence<sup>11</sup> suggests that, at least in some cases, reversible formation of a radical pair ( $R-N=N-R \rightleftharpoons R-N_2\cdot + R\cdot$ ) may precede the final fission.

Perhaps because of these mechanistic uncertainties, different reactivity orders were found in the peresters<sup>8</sup> than among the azo compounds.<sup>6,7</sup> The former followed a partial reactivity order of  $C_5 < C_6 < C_7 < C_8$ , with a very small spread in rates, whereas the azo compounds gave the order  $C_6 < C_5 \approx C_7 < C_8$ , similar to the relative rates of carbonium ion formation in the corresponding cycloalkyl chlorides.<sup>3</sup>

In a review,<sup>7</sup> Rüchardt discussed the consequences of steric effects in free-radical reactions. The conventional explanation<sup>12</sup> of the usual reactivity order, primary < secondary < tertiary, of the ease of forming free radicals is that successive alkyl substitution at the radical center increases radical stability by inductive or hyperconjugative effects. Consistent with this view, bond dissociation energies<sup>7,13</sup> decrease through typical series  $CH_3-X$  to  $(CH_3)_3C-X$ , and esr studies<sup>14</sup> show that methyl substitution reduces the spin density on the central carbon atom. Rüchardt challenged this viewpoint, which emphasizes the increasing stability of radicals primary < secondary < tertiary, and implies that the parent alkyl derivatives are insensitive to alkyl substitution; he argued that the bond-

energy data are equally compatible with the radicals being all of comparable energy, while steric compression, resulting from increased alkyl substitution, makes the parent alkyl compounds progressively less stable.

In this paper are reported relative rates of free-radical hydrogen abstraction from cycloalkanes of ring size  $C_5$ - $C_{12}$ . We sought to establish the stability order of the corresponding cycloalkyl radicals as a function of ring size through the use of the mechanistically unambiguous reaction of hydrogen abstraction; since all C-H bonds in this series are secondary, only conformational effects should be involved. In addition, by comparing the ease of hydrogen abstraction in this series with open-chain primary, secondary, and tertiary positions, we hoped to be able to evaluate the postulate that steric factors are all-important in determining free-radical reactivities.

**Reversible Hydrogen Abstraction.** Our first objective was to demonstrate that hydrogen abstraction would occur irreversibly for all the abstracting agents used: reversible hydrogen abstraction gives apparent relative rate constants that are usually exaggerated in favor of abstraction from the more reactive substrate.<sup>15</sup> Following are our criteria for irreversible abstraction by each of the abstracting agents used, *viz.*,  $Cl\cdot$ , *t*-BuO $\cdot$ ,  $C_6H_5\cdot$ ,  $Br\cdot$ , and  $CCl_3\cdot$ .

$Cl\cdot$ . Hydrogen abstraction by chlorine atoms is exothermic, and is irreversible in chlorinations,<sup>16</sup> except in unusual circumstances.<sup>15</sup>

*t*-BuO $\cdot$ . Hydrogen abstraction from aliphatic substrates during chlorinations by *tert*-butyl hypochlorite is effected exclusively by *tert*-butoxy radicals, and is kinetically irreversible.<sup>17,18</sup> We demonstrated the absence of chlorine atom chains by carrying out some of our reactions in the presence of trichloroethylene, which acts as a chlorine atom trap.<sup>17</sup> Except in one case, noted in Table II, the experimental results were insensitive to the addition of trichloroethylene to the reaction mixtures.

$C_6H_5\cdot$ . The extreme inertness of benzene toward hydrogen abstraction shows the irreversibility of abstraction by the phenyl radical.<sup>19</sup> In reactions involving benzoyl peroxide, there is the possibility of abstraction by benzoate radicals, the immediate precursors of phenyl radicals. This seems unlikely in that Bevington and Lewis<sup>20</sup> showed that at the temperature we used, benzoate radicals decarboxylate faster than they add to styrene, a reaction of low activation energy;<sup>21</sup> hence decarboxylation is probably also faster than hydrogen abstraction.

$Br\cdot$ . Bromine atom abstractions are endothermic and are well known to be easily reversible.<sup>22-24</sup> *N*-Bromosuccinimide (NBS) brominates by way of a bromine atom chain,<sup>25</sup> but hydrogen bromide is removed as it is formed by reaction with NBS.<sup>25,26</sup> In homogeneous acetonitrile

**Table I**  
Relative Reactivities per Molecule of Alkanes with Various Abstracting Radicals<sup>a</sup>

R <sup>1</sup> H	R <sup>2</sup> H	R <sup>3</sup> H	Inert reference	Vpc	No. of reac- tions	Temp, °C	$k_2/k_1$	$k_3/k_1$
Chlorine Atom Abstraction, Cl <sub>2</sub> /CCl <sub>4</sub> /hν								
C <sub>6</sub> H <sub>14</sub>	C <sub>5</sub> H <sub>10</sub>		F <sub>113</sub> <sup>b</sup>	SE-30, 45°	6	0	0.970 ± 0.009	
C <sub>6</sub> H <sub>14</sub>	C <sub>5</sub> H <sub>10</sub>		F <sub>113</sub>	SE-30, 45°	6	49.5	0.992 ± 0.009	
C <sub>6</sub> H <sub>14</sub>	C <sub>6</sub> H <sub>12</sub>		F <sub>113</sub>	DIDP, 60° <sup>c</sup>	3	0	1.013 ± 0.008	
C <sub>6</sub> H <sub>14</sub>	C <sub>6</sub> H <sub>12</sub>		F <sub>113</sub>	DIDP, 60°	3	49.5	1.056 ± 0.009	
C <sub>8</sub> H <sub>18</sub>	C <sub>6</sub> H <sub>12</sub>	C <sub>7</sub> H <sub>14</sub>	F <sub>112</sub>	DIDP, 70°	3	0	0.955 ± 0.006	1.021 ± 0.010
C <sub>8</sub> H <sub>18</sub>	C <sub>6</sub> H <sub>12</sub>	C <sub>7</sub> H <sub>14</sub>	F <sub>112</sub>	DIDP, 70°	3	49.5	0.931 ± 0.003	1.003 ± 0.009
C <sub>7</sub> H <sub>14</sub>	C <sub>8</sub> H <sub>16</sub>		C <sub>6</sub> H <sub>5</sub> Cl	SE-30, 110°	3	0	1.091 ± 0.007	
C <sub>7</sub> H <sub>14</sub>	C <sub>8</sub> H <sub>16</sub>		C <sub>6</sub> H <sub>5</sub> Cl	SE-30, 110°	3	49.5	1.065 ± 0.008	
C <sub>10</sub> H <sub>22</sub>	C <sub>8</sub> H <sub>16</sub>	C <sub>10</sub> H <sub>20</sub>	C <sub>2</sub> Cl <sub>6</sub>	SE-30, 150°	6	0	0.981 ± 0.017	0.929 ± 0.027
C <sub>10</sub> H <sub>22</sub>	C <sub>8</sub> H <sub>16</sub>	C <sub>10</sub> H <sub>20</sub>	C <sub>2</sub> Cl <sub>6</sub>	SE-30, 150°	4	49.5	0.959 ± 0.009	0.888 ± 0.004
C <sub>10</sub> H <sub>20</sub>	C <sub>12</sub> H <sub>24</sub>		C <sub>2</sub> Cl <sub>6</sub>	SE-30, 185°	5	0	1.016 ± 0.014	
C <sub>10</sub> H <sub>20</sub>	C <sub>12</sub> H <sub>24</sub>		C <sub>2</sub> Cl <sub>6</sub>	SE-30, 185°	3	49.5	1.035 ± 0.021	
<i>tert</i> -Butoxy Radical Abstraction, C <sub>4</sub> H <sub>9</sub> OCl/CCl <sub>4</sub> /hν								
C <sub>6</sub> H <sub>14</sub>	C <sub>5</sub> H <sub>10</sub>	C <sub>6</sub> H <sub>12</sub>	F <sub>113</sub>	DIDP, 50°	3	0	1.661 ± 0.008	2.047 ± 0.013
C <sub>6</sub> H <sub>14</sub>	C <sub>5</sub> H <sub>10</sub>	C <sub>6</sub> H <sub>12</sub>	F <sub>113</sub>	DIDP, 50°	3	49.5	1.527 ± 0.009	1.898 ± 0.044
C <sub>8</sub> H <sub>18</sub>	C <sub>6</sub> H <sub>12</sub>	C <sub>7</sub> H <sub>14</sub>	F <sub>112</sub>	DIDP, 70°	3	0	1.377 ± 0.018	2.402 ± 0.017
C <sub>8</sub> H <sub>18</sub>	C <sub>6</sub> H <sub>12</sub>	C <sub>7</sub> H <sub>14</sub>	F <sub>112</sub>	DIDP, 70°	3	49.5	1.391 ± 0.024	2.163 ± 0.025
C <sub>7</sub> H <sub>14</sub>	C <sub>8</sub> H <sub>16</sub>		C <sub>6</sub> H <sub>5</sub> Cl	SE-30, 110°	3	0	1.294 ± 0.016	
C <sub>7</sub> H <sub>14</sub>	C <sub>8</sub> H <sub>16</sub>		C <sub>6</sub> H <sub>5</sub> Cl	SE-30, 110°	3	49.5	1.244 ± 0.011	
C <sub>10</sub> H <sub>22</sub>	C <sub>8</sub> H <sub>16</sub>	C <sub>10</sub> H <sub>20</sub>	C <sub>2</sub> Cl <sub>6</sub>	DIDP, 130°	3	0	2.397 ± 0.018	2.356 ± 0.029
C <sub>10</sub> H <sub>22</sub>	C <sub>8</sub> H <sub>16</sub>	C <sub>10</sub> H <sub>20</sub>	C <sub>2</sub> Cl <sub>6</sub>	DIDP, 130°	3	49.5	2.004 ± 0.007	1.575 ± 0.086
C <sub>10</sub> H <sub>20</sub>	C <sub>12</sub> H <sub>24</sub>		C <sub>2</sub> Cl <sub>6</sub>	DIDP, 140°	3	0	0.861 ± 0.007	
C <sub>10</sub> H <sub>20</sub>	C <sub>12</sub> H <sub>24</sub>		C <sub>2</sub> Cl <sub>6</sub>	DIDP, 140°	3	49.5	0.925 ± 0.010	
Phenyl Radical Abstraction, Bz <sub>2</sub> O <sub>2</sub> /CH <sub>3</sub> CN								
C <sub>6</sub> H <sub>14</sub>	C <sub>5</sub> H <sub>10</sub>	C <sub>6</sub> H <sub>12</sub>	F <sub>113</sub>	DIDP, 55°	3	74.5	1.731 ± 0.019	0.739 ± 0.024
C <sub>8</sub> H <sub>18</sub>	C <sub>7</sub> H <sub>14</sub>	C <sub>8</sub> H <sub>16</sub>	C <sub>6</sub> H <sub>5</sub> Cl	DIDP, 75°	3	74.5	2.63 ± 0.05	4.20 ± 0.12
C <sub>10</sub> H <sub>22</sub>	C <sub>8</sub> H <sub>16</sub>	C <sub>10</sub> H <sub>20</sub>	<i>p</i> -C <sub>6</sub> H <sub>4</sub> Cl <sub>2</sub>	DIDP, 145°	3	74.5	4.11 ± 0.12	4.21 ± 0.17
C <sub>10</sub> H <sub>20</sub>	C <sub>12</sub> H <sub>24</sub>		<i>p</i> -C <sub>6</sub> H <sub>4</sub> Cl <sub>2</sub>	DIDP, 155°	3	74.5	0.363 ± 0.011	
Trichloromethyl Radical Abstraction, CCl <sub>3</sub> Br/CH <sub>3</sub> CN/Bz <sub>2</sub> O <sub>2</sub>								
C <sub>6</sub> H <sub>14</sub>	C <sub>5</sub> H <sub>10</sub>	C <sub>6</sub> H <sub>12</sub>	F <sub>113</sub>	DIDP, 55°	3	74.5	1.79 ± 0.06	1.43 ± 0.03
C <sub>10</sub> H <sub>22</sub>	C <sub>8</sub> H <sub>16</sub>	C <sub>10</sub> H <sub>20</sub>	<i>p</i> -C <sub>6</sub> H <sub>4</sub> Cl <sub>2</sub>	DIDP, 145°	3	74.5	3.54 ± 0.05	3.16 ± 0.09
C <sub>10</sub> H <sub>20</sub>	C <sub>12</sub> H <sub>24</sub>		<i>p</i> -C <sub>6</sub> H <sub>4</sub> Cl <sub>2</sub>	DIDP, 150°	3	74.5	0.52 ± 0.02	
Trichloromethyl Radical Abstraction, CCl <sub>3</sub> Br/CCl <sub>4</sub> /Bz <sub>2</sub> O <sub>2</sub>								
C <sub>6</sub> H <sub>14</sub>	C <sub>5</sub> H <sub>10</sub>	C <sub>6</sub> H <sub>12</sub>	F <sub>113</sub>	DIDP, 55°	6	74.5	2.19 ± 0.04	0.65 ± 0.04
C <sub>10</sub> H <sub>22</sub>	C <sub>8</sub> H <sub>16</sub>	C <sub>10</sub> H <sub>20</sub>	<i>p</i> -C <sub>6</sub> H <sub>4</sub> Cl <sub>2</sub>	DIDP, 145°	3	74.5	5.10 ± 0.17	5.88 ± 0.26
C <sub>10</sub> H <sub>20</sub>	C <sub>12</sub> H <sub>24</sub>		<i>p</i> -C <sub>6</sub> H <sub>4</sub> Cl <sub>2</sub>	DIDP, 155°	3	74.5	0.49 ± 0.02	
Bromine Atom Abstraction, NBS/CH <sub>3</sub> CN, Bz <sub>2</sub> O <sub>2</sub> , or <i>t</i> -Bu <sub>2</sub> O <sub>2</sub>								
C <sub>6</sub> H <sub>14</sub>	C <sub>5</sub> H <sub>10</sub>	C <sub>6</sub> H <sub>12</sub>	F <sub>113</sub>	DIDP, 55°	3	74.5	1.843 ± 0.031	0.710 ± 0.015
C <sub>6</sub> H <sub>14</sub>	C <sub>5</sub> H <sub>10</sub>	C <sub>6</sub> H <sub>12</sub>	F <sub>113</sub>	DIDP, 55°	3	124.5	1.640 ± 0.050	1.021 ± 0.05
C <sub>8</sub> H <sub>18</sub>	C <sub>7</sub> H <sub>14</sub>	C <sub>8</sub> H <sub>16</sub>	C <sub>6</sub> H <sub>5</sub> Cl	DIDP, 75°	3	74.5	3.79 ± 0.12	11.25 ± 0.32
C <sub>8</sub> H <sub>18</sub>	C <sub>7</sub> H <sub>14</sub>	C <sub>8</sub> H <sub>16</sub>	C <sub>6</sub> H <sub>5</sub> Cl	DIDP, 75°	3	124.5	3.31 ± 0.39	7.41 ± 1.5
C <sub>10</sub> H <sub>22</sub>	C <sub>8</sub> H <sub>16</sub>	C <sub>10</sub> H <sub>20</sub>	<i>p</i> -C <sub>6</sub> H <sub>4</sub> Cl <sub>2</sub>	DIDP, 145°	6	74.5	4.82 ± 0.33	8.49 ± 0.60
C <sub>10</sub> H <sub>22</sub>	C <sub>8</sub> H <sub>16</sub>	C <sub>10</sub> H <sub>20</sub>	<i>p</i> -C <sub>6</sub> H <sub>4</sub> Cl <sub>2</sub>	DIDP, 150°	3	124.5	3.17 ± 0.10	5.07 ± 0.19
C <sub>10</sub> H <sub>20</sub>	C <sub>12</sub> H <sub>24</sub>		<i>p</i> -C <sub>6</sub> H <sub>4</sub> Cl <sub>2</sub>	DIDP, 155°	3	74.5	0.137 ± 0.01	
C <sub>10</sub> H <sub>20</sub>	C <sub>12</sub> H <sub>24</sub>		<i>p</i> -C <sub>6</sub> H <sub>4</sub> Cl <sub>2</sub>	DIDP, 155°	3	124.5	0.235 ± 0.006	

<sup>a</sup> Concentrations of substrates were ~0.5 M except where acetonitrile was the solvent, when lower concentrations were necessary for homogeneous solutions. <sup>b</sup> F<sub>113</sub> and F<sub>112</sub> are Freon 113 (1,1,2-trifluoro-1,2,2-trichloroethane) and Freon 112 (1,2-difluoro-1,1,2,2-tetrachloroethane), respectively. <sup>c</sup> Diisodecyl phthalate.

solutions, NBS brominations have been shown to be essentially irreversible.<sup>27</sup>

CCl<sub>3</sub>·. This radical is the hydrogen abstractor in brominations using bromotrichloromethane;<sup>28,29</sup> it was not known whether the abstraction was irreversible, though the high selectivity of the reaction and its near thermoneutrality<sup>30</sup> made the possibility not unlikely. Huyser<sup>31</sup> found small amounts of HBr among the products of the photoreaction of CCl<sub>3</sub>Br with toluene; since abstraction from HBr is so facile, abstraction would be expected to be reversible under these conditions. Accordingly, photoinitiated reactions of CCl<sub>3</sub>Br with a mixture of cyclohexane and cyclohexane-*d*<sub>12</sub> led to almost complete isotopic

scrambling between the two substrates. However, similar reactions initiated by benzoyl peroxide showed no exchange; since no bromine atoms (and hence HBr) are formed in the peroxide-initiated reactions, these results imply that the exchange was due to the incursion of bromine atom chains and that abstraction by the trichloromethyl radical is irreversible. In support of this conclusion, peroxide-initiated reactions of CCl<sub>3</sub>Br or CCl<sub>4</sub> with cyclohexane in the presence of CDCl<sub>3</sub>, or with cyclohexane-*d*<sub>12</sub> in the presence of CHCl<sub>3</sub>, led to no incorporation of the "other" hydrogen isotope into the unreacted cyclohexane. Presumably the extreme polar deactivation of chloroform is the cause of the high activation energy for

**Table II**  
Relative Selectivity per Hydrogen for Hydrogen Atom  
Abstraction from Hexane and 2,3-Dimethylbutane

System	Run 1		Run 2	
	Temp, °C	Rel selectivity	Temp, °C	Rel selectivity
Cl <sub>2</sub> /hexane/CCl <sub>4</sub> /hν	0	2.62 ± 0.01 (3) <sup>a</sup>	0	2.46 ± 0.01 (4)
	49.5	2.31 ± 0.01 (3)	24.5	2.34 ± 0.01 (4)
			41.0	2.28 ± 0.01 (4)
Cl <sub>2</sub> /dimethylbutane/CCl <sub>4</sub> /hν	0	3.80 ± 0.02 (4)		
	27.5	3.48 ± 0.02 (4)		
	45.5	3.35 ± 0.02 (4)		
<i>t</i> -BuOCl/hexane/hν <sup>b</sup>	0	8.07 ± 0.15 (3)	0	8.34 ± 0.16 (5)
	49.5	5.66 ± 0.11 (3)	23.5	7.54 ± 0.05 (4)
			45.5	6.72 ± 0.04 (5)
<i>t</i> -BuOCl/dimethylbutane/hν <sup>c</sup>	0	60.4 ± 0.4 (5)	0	64.6 ± 0.9 (3)
	27.3	52.1 ± 0.7 (2)	27.5	54.8 ± 0.9 (4)
	46.3	42.1 ± 0.4 (3)	45.5	47.3 ± 0.2 (4)

<sup>a</sup> Numbers in parentheses are the numbers of independent experiments. <sup>b</sup> Reactions were unaffected by adding C<sub>2</sub>HCl<sub>3</sub>. <sup>c</sup> Run 1: no C<sub>2</sub>HCl<sub>3</sub>; run 2: 100 mol % C<sub>2</sub>HCl<sub>3</sub> added.

**Table III**  
Chlorination of Cyclohexane by Carbon Tetrachloride<sup>a</sup>

Reactants					Products <sup>b</sup>		
CCl <sub>4</sub>	C <sub>6</sub> H <sub>12</sub>	CDCl <sub>3</sub>	Bz <sub>2</sub> O <sub>2</sub>	CH <sub>2</sub> Cl <sub>2</sub>	C <sub>6</sub> H <sub>6</sub>	CHCl <sub>3</sub> <sup>c</sup>	C <sub>6</sub> H <sub>11</sub> Cl <sup>d</sup>
1.92	2.37	8.16	0.12	0.278	0.13	0.48	0.56
1.97	2.33	8.52	0.11	0.245	0.08	0.31	0.32
1.98	2.40	8.30	0.12	0.303	0.16	0.61	0.79

<sup>a</sup> All quantities are in millimoles. <sup>b</sup> Determined by nmr relative to CH<sub>2</sub>Cl<sub>2</sub>. <sup>c</sup> Corrected for <sup>1</sup>H in starting CDCl<sub>3</sub>. <sup>d</sup> Estimated from the area of the tertiary hydrogen at δ 3.89.

both forward and reverse reactions,<sup>29</sup> so that even in the short-chain reaction with CCl<sub>4</sub> (see Table III) chain transfer with CCl<sub>4</sub> always competes successfully with hydrogen abstraction from chloroform. Tanner's group, in a detailed study of the reaction between bromotrichloromethane and substituted toluenes, have recently concluded that benzylic hydrogen abstraction by the trichloromethyl radical is also irreversible.<sup>32</sup>

### Experimental Section

The alkanes and cycloalkanes were high-purity commercial products, checked by vpc for impurities before use. Cyclohexane-*d*<sub>12</sub> was obtained from Stohler Isotope Chemicals. Benzoyl peroxide, NBS, and CCl<sub>3</sub>Br were commercial products; *tert*-butyl hypochlorite was prepared by the method of Teeter and Bell,<sup>33</sup> and was always freshly distilled before use.

Reactions were run in sealed Pyrex glass ampoules, which were evacuated by freeze-thaw cycles, and then placed in thermostated baths whose temperatures were controlled to at least ±0.3°. Chlorinations using elemental chlorine were photoinitiated by the diffuse light of the room; *tert*-butyl hypochlorite reactions were photoinitiated by two 60-W tungsten lamps. Reactions near 75° were initiated by benzoyl peroxide, those near 125° by di-*tert*-butyl peroxide. Brominations involving NBS were carried out in homogeneous solution in acetonitrile, which was purified by the method of Forcier and Olver.<sup>34</sup> A specific impurity removed by this procedure is acrylonitrile, which acts as a free-radical trap.

Relative reactivities per molecule were determined by the competition method, in which a limited amount of the abstracting reagent competes for two different substrates RH and SH, using the relationship  $k_{RH}/k_{SH} = \log(RH_i/RH_f)/\log(SH_i/SH_f)$ , where subscripts *i* and *f* refer to initial and final concentrations. Concentrations were determined by vpc (Varian Aerograph Model 90P3), by comparing the peak areas due to RH and SH with that of an unreactive standard compound added to the reaction mixture. Relative selectivities for attack at different sites within the same molecule were estimated from the yields of isomeric products resulting from attack of the reagent upon a large excess of substrate.

At least three vpc analyses were made for each reaction mixture, and several independent reactions were carried out for each competition or selectivity. Peak areas were taken to be the product of peak height and the width at half height, and for relative

selectivity experiments, the response of the gas chromatograph was assumed to be equal toward isomers. Deviations from the mean were estimated by the approximate formula  $\pm = \Sigma d/[n(n-1)^{1/2}]$  where *d* is the deviation of each measurement from the mean and *n* is the number of independent experiments.<sup>35</sup> The results of the competition and relative selectivity experiments are given in Tables I and II.

**Reaction of CCl<sub>3</sub>Br with C<sub>6</sub>H<sub>12</sub> and C<sub>6</sub>D<sub>12</sub>.** The alkane mixture comprised cyclohexane-*d*<sub>0</sub> (0.751 g) and cyclohexane-*d*<sub>12</sub> (0.823 g). For the photoinitiated reactions three reaction mixtures were prepared, each containing the alkane mixture (0.15 ml) and bromotrichloromethane (0.5 ml). The evacuated ampoules were irradiated for 48 hr at ambient temperature using a 500-W Hanovia mercury arc lamp cooled by an immersion well and placed about 2 in. from the reaction ampoules. Analysis by gc-mass spectrometry<sup>36</sup> of the cyclohexane remaining in the mixtures indicated that the molecular ions due to C<sub>6</sub>H<sub>12</sub> (*m/e* 84) and C<sub>6</sub>D<sub>12</sub> (*m/e* 96) were now entirely absent, and that the most abundant molecular ions appeared in the range *m/e* 88–92.

Peroxide-initiated reactions employed the alkane mixture (0.15 ml), bromotrichloromethane (0.1 ml), and benzoyl peroxide (60 mg). The evacuated ampoules were heated to 90° for 20 hr; analysis of the unreacted cyclohexane by gc-mass spectrometry in this case showed no change in the abundance of *m*<sup>+</sup>/*e* 85 and 86 relative to 84 or of *m*<sup>+</sup>/*e* 94 and 95 relative to 96. Similar results were obtained in reactions where CCl<sub>4</sub> was used as the source of trichloromethyl radicals instead of CCl<sub>3</sub>Br.

**Reaction of CCl<sub>4</sub> with Cyclohexane in the Presence of CDCl<sub>3</sub>.** Sealed evacuated ampoules containing carbon tetrachloride, cyclohexane, deuteriochloroform, and benzoyl peroxide in the quantities indicated in Table III were heated to 98° for 1.5 hr. After the reaction, methylene chloride was added to each reaction mixture as a standard; and the mixtures were analyzed by nmr. Gc-mass spectrometric analysis indicated that no deuterium had been incorporated into the cyclohexane.

Similar reaction mixtures containing CCl<sub>3</sub>Br instead of CCl<sub>4</sub> were analyzed by gc-mass spectrometry only. They, too, showed no incorporation of deuterium into the unreacted cyclohexane.

Reactions involving CCl<sub>4</sub> and cyclohexane-*d*<sub>12</sub> in the presence of CHCl<sub>3</sub> were also carried out. In these experiments, three 1.0-ml aliquots were withdrawn from a mixture of carbon tetrachloride (6.49 mmol), perdeuteriocyclohexane (7.99 mmol), chloroform (37.8 mmol), and benzoyl peroxide (0.70 mmol), and the solutions were heated in sealed evacuated ampoules for 1 hr at 98°. The remaining solution was stored at -15°. Methylene chloride was now added to both the control solution and the reaction mixtures, and

**Table IV**  
**Mean Reactivities per Methylene Group of Cycloalkanes toward Radicals**  
**Relative to Open-Chain Methylene Groups**

Radical, conditions	C <sub>5</sub>	C <sub>6</sub>	C <sub>7</sub>	C <sub>8</sub>	C <sub>10</sub>	C <sub>12</sub>
Cl·, Cl <sub>2</sub> /CCl <sub>4</sub> , 0°	1.00	1.00	1.04	1.06	0.85	0.72
Cl·, Cl <sub>2</sub> /CCl <sub>4</sub> , 49.5°	1.05	1.02	1.05	1.02	0.83	0.71
Cl·, Cl <sub>2</sub> /CCl <sub>4</sub> , 40°, ref 38	1.04	(1) <sup>a</sup>	1.11	1.59		
<i>t</i> -BuO·, <i>t</i> -BuOCl, CCl <sub>4</sub> , 0°	1.45	1.47	2.19	2.49	1.97	1.52
<i>t</i> -BuO·, <i>t</i> -BuOCl, CCl <sub>4</sub> , 49.5°	1.38	1.47	2.01	2.16	1.34	1.03
<i>t</i> -BuO·, <i>t</i> -BuOCl, 40°, ref 39	1.38	1.50				
C <sub>6</sub> H <sub>5</sub> ·, Bz <sub>2</sub> O <sub>2</sub> , CH <sub>3</sub> CN, 74.5°	1.50	0.53	2.37	3.80	3.51	1.06
C <sub>6</sub> H <sub>5</sub> ·, PAT, CCl <sub>4</sub> , 60°, ref 40	1.14	0.99	1.80	1.98		
CCl <sub>3</sub> ·, CCl <sub>3</sub> Br, CH <sub>3</sub> CN, 74.5°	1.43	0.95		3.54	2.53	1.11
CCl <sub>3</sub> ·, CCl <sub>3</sub> Br, CCl <sub>4</sub> , 74.5°	1.75	0.43		5.10	4.70	1.92
CCl <sub>3</sub> ·, CCl <sub>3</sub> Br, 80°, ref 41	1.88	(1) <sup>a</sup>	2.83	6.89		
CCl <sub>3</sub> ·, CCl <sub>3</sub> Br, gas phase, 247°, ref 29	1.60	(1) <sup>a</sup>	4.20	6.00		
Br·, NBS, CH <sub>3</sub> CN, 74.5°	1.47	0.47	3.25	6.63	6.79	0.97
Br·, NBS, CH <sub>3</sub> CN, 124.5°	1.31	0.70	2.83	4.37	4.05	0.79
Comparative Data						
Cycloalkaneazobitrile decomposition, 80° (ref 6)	11.5	(1) <sup>a</sup>	194	1325	292	
Cycloalkanecarboxylic peresters, 110° (ref 8)	0.47	(1) <sup>a</sup>	2.27	4.26	3.26	1.91
1-Methylcycloalkyl chloride solvolysis, <sup>b</sup> 80° (ref 3b)	43.7	0.35	38.0	100	6.22	

<sup>a</sup> Assumed. <sup>b</sup> Relative to *tert*-butyl chloride.

the solutions were analyzed by nmr and gc-mass spectrometry. No incorporation of <sup>3</sup>H hydrogen into the perdeuteriocyclohexane was observed.

### Discussion

The raw relative rates of Table I are given in Table IV as relative rates per CH<sub>2</sub> group compared in each case with the average of the methylene positions of hexane as standard, and including comparative literature values where available. The relative reactivities of the linear reference substrates were corrected for reaction at the terminal, primary hydrogens, making the assumption<sup>37</sup> that the relative selectivity primary:secondary was independent of chain length. The necessary relative selectivities were taken from Table II for chlorine atoms and *tert*-butoxy radicals; for trichloromethyl radicals, phenyl radicals, and bromine atoms, literature data were used.<sup>28,40,42</sup>

The reactivities generally follow the order of solvolyses of the azocycloalkanes,<sup>6,7</sup> rather than that of the peresters.<sup>8</sup> Naturally, the spread in reactivities is governed by radicals. They thus accord with the decomposition order of the azocycloalkanes,<sup>6,7</sup> rather than that of the peresters.<sup>8</sup> Naturally, the spread in reactivities is governed by the abstracting radical; it is small for a reactive radical like Cl· where little bond breaking has occurred at the transition state, and larger for the endothermic abstraction by bromine atoms. The apparent different range of reactivities observed with CCl<sub>3</sub>· in carbon tetrachloride and acetonitrile seems interesting, but owing to the difficulty of being sure to have eliminated entirely reversible hydrogen abstraction, we do not at this time regard it as an established solvent effect. The overall reactivity orders of the cycloalkanes are in satisfactory agreement with the selectivity ratios established<sup>7</sup> for the discrimination of cycloalkyl radicals toward abstraction of Br or Cl from BrCCl<sub>3</sub>-CCl<sub>4</sub>. Selectivity is often the inverse of reactivity, so that it would be expected that a radical more easily formed would tend to be less reactive. Comparison of our data with those of Table 8, ref 7, shows this indeed to be the case.

Activation parameters have been obtained from our data for Cl·, *t*-BuO·, and Br· as abstracting radicals and are given in Table V, though since determinations

were made at but two temperatures, we regard them as only qualitative. Even so, they afford some insight into the origins of the reactivity differences among the cycloalkanes. We consider first the group cyclopentane (C<sub>5</sub>), hexane (*n*-C<sub>6</sub>), cyclohexane (C<sub>6</sub>), and cycloheptane (C<sub>7</sub>), where the present results may be compared with extensive gas-phase data that have appeared since the outset of this work.<sup>29,43-46</sup> The similarity with the gas-phase results rules out solvation effects as predominant in these systems, and the dependence of reactivity upon activation energies clearly reflects the influence of bond dissociation energy on the energy of the transition state.

For chlorine atom abstractions, activation energy differences are insignificantly small within the precision of our experiments, and since the transition state for hydrogen removal by chlorine atoms occurs early in the reaction, these activation parameters probably provide little information about the relative stabilities of the cycloalkyl radicals. With bromine atoms, the order of activation energies is C<sub>5</sub> ≈ C<sub>7</sub> < *n*-C<sub>6</sub> < C<sub>6</sub>. This may be explained in conventional conformational terms: cyclohexane has perfect tetrahedral geometry, so that strain is introduced into the ring when one of the carbon atoms becomes sp<sup>2</sup> hybridized; for the all-eclipsed cyclopentane and the somewhat overcrowded cycloheptane, removal of one hydrogen atom and rehybridization relieves strain. This is the reasoning used to explain the relative ease of formation of cycloalkyl cations<sup>3,5</sup> and the reactivity order of azocycloalkane decompositions.<sup>6,7</sup> The only objection to this argument is the recent claim by Furuyama, *et al.*,<sup>44</sup> that cyclopentane and the cyclopentyl radical have the same strain energy, *i.e.*, that removal of the hydrogen atom does not relieve strain. The activation energy order C<sub>7</sub> ≈ C<sub>5</sub> < *n*-C<sub>6</sub> ≈ C<sub>6</sub> in the *tert*-butoxy series may be explained similarly.

For the larger cycloalkanes our solution data extend the previous gas-phase results. Compared with open-chain positions, hydrogen abstraction in the C<sub>8</sub>-C<sub>12</sub> rings is attended by a lower activation energy, but the expected enhancement of the reactivity of these compounds is at least partly offset by the decrease in the preexponential factor. Cyclooctane and cyclodecane particularly are known to be overcrowded,<sup>47</sup> so that removal of a hydrogen atom re-

Table V  
Activation Parameters for Hydrogen Abstraction from Cycloalkanes  
Relative to Open-Chain Methylene Groups

Substrate	Cl·		t-BuO·		Br·	
	$E - E_0$	$\text{Log } A/A_0$	$E - E_0$	$\text{Log } A/A_0$	$E - E_0$	$\text{Log } A/A_0$
C <sub>5</sub>	+0.19	+0.15	-0.17	+0.02	-0.63	-0.23
C <sub>6</sub>	+0.07	+0.05	-0.02	+0.15	+2.19	+1.04
C <sub>7</sub>	+0.03	+0.04	-0.30	+0.10	-0.76	+0.05
C <sub>8</sub>	-0.12	-0.07	-0.52	-0.02	-2.23	-0.60
C <sub>10</sub>	-0.10	-0.15	-1.35	-0.79	-2.82	-0.92
C <sub>12</sub>	-0.04	-0.17	-1.38	-0.92	-1.12	-0.72

Table VI  
Activation Parameters for Abstraction of Primary,  
Secondary, and Tertiary Hydrogens in  
Open-Chain Systems

Radical	$E_p - E_s$	$\text{Log } A_p/A_s$	$E_p - E_t$	$\text{Log } A_p/A_t$
Cl·	0.46	0.06	0.48	0.20
	0.31	0.14	0.82 <sup>a</sup>	0.02 <sup>a</sup>
t-BuO·	1.33	-0.13	1.35	0.72
	0.91	+0.21	1.35	0.74
	1.54 <sup>b</sup>	-0.12 <sup>b</sup>	1.85 <sup>b</sup>	0.35 <sup>b</sup>
	0.93 <sup>b</sup>	+0.36 <sup>b</sup>		
Br·	4.14 <sup>c</sup>	-0.22 <sup>c</sup>		
	4.06 <sup>c</sup>	-0.43 <sup>c</sup>	6.58 <sup>c</sup>	-0.11 <sup>c</sup>

<sup>a</sup> Reference 38. <sup>b</sup> Reference 49. <sup>c</sup> Reference 50.

lieves strain. The lower preexponential factor, which is observed even for attack of chlorine atoms, presumably reflects the difficulty of close approach of the abstracting radical to these sterically encumbered and sometimes inaccessible hydrogen atoms. If we use the Evans-Polanyi relationship (admittedly based on gas-phase data) of Ferguson and Whittle,<sup>43</sup> viz.,  $E_{Br} = 0.87[D(R-H) - 82.7]$ , we may estimate the previously unreported bond dissociation energies of the C<sub>8</sub>, C<sub>10</sub>, and C<sub>12</sub> cycloalkanes. The values obtained are of course very approximate, but suggest bond dissociation energies in the neighborhood of 93, 93, and 94 kcal/mol, respectively, based upon 95.0 kcal/mol for typical open-chain methylene positions,<sup>48</sup> though based upon a bond dissociation energy of 95.5 kcal/mol for cyclohexane,<sup>43</sup> they would be lower still.

Finally, we address ourselves to the question of whether steric compression of alkanes can be responsible for the primary < secondary < tertiary reactivity order in free-radical reactions of open-chain systems. We have compared activation energies among the cycloalkanes (Table V), where variations have to be construed broadly as steric in origin, with those for open-chain positions (Table VI). Even though transannular overcrowding of the larger rings in the series is a feature special to these systems, and does not occur in open-chain systems, the activation energy spread is much smaller than that observed in primary, secondary, and tertiary open-chain systems. Thus, even in those cyclic systems where steric problems are maximized, the spread in activation energies is still smaller than that observed in open systems, suggesting that factors additional to steric effects must be invoked to explain reactivity differences in open-chain systems.

**Acknowledgments.** The authors wish to thank the National Research Council of Canada for financial support, and to acknowledge generous gifts of cyclodecane by Cities Service Co. and of Freon 112 by E. I. du Pont de Nemours and Co.

**Registry No.**—C<sub>6</sub>H<sub>14</sub>, 110-54-3; C<sub>5</sub>H<sub>10</sub>, 287-92-3; C<sub>6</sub>H<sub>12</sub>, 110-82-7; C<sub>8</sub>H<sub>18</sub>, 111-65-9; C<sub>7</sub>H<sub>14</sub>, 291-64-5; C<sub>8</sub>H<sub>16</sub>, 292-64-8; C<sub>10</sub>H<sub>22</sub>, 124-18-5; C<sub>10</sub>H<sub>20</sub>, 293-96-9; C<sub>12</sub>H<sub>24</sub>, 294-62-2; Cl radical, 22537-15-1; tert-butoxy radical, 3141-58-0; phenyl radical, 2396-01-2; tri-

chloromethyl radical, 3170-80-7; Br radical, 10097-32-2; 2,3-dimethylbutane, 79-29-8.

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- This assumption does not hold uniformly well, in that relative reactivities based on different reference substrates are not always

- within the desired 1 or 2% agreement. However, the values of  $\Delta E_{\text{act}}$  obtained agree well, whichever value is used. One problem we encountered was the possibility of systematic error in the vpc analysis. Thus experiments, for example selectivities in Table II, frequently exhibited excellent reproducibility within a series, but sets of experiments run at different times, or using slightly different vpc conditions, varied noticeably from set to set.
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## Ring Strain Effects. IV.<sup>1</sup> An Electron Spin Resonance Study of the Radical Anions of a Series of Strained Naphthalene Hydrocarbons

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Received December 7, 1973

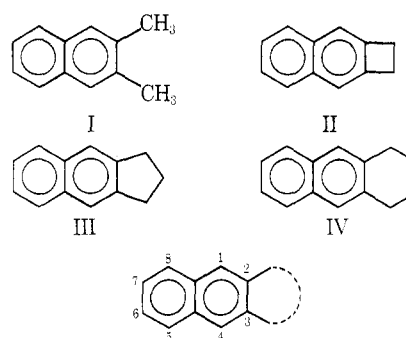
Electron paramagnetic resonance studies have been carried out on a series of substituted naphthalene radical anions. The series was composed of compounds having varying amounts of ring strain in a fused ring in the *b* position. The large spin density perturbations were correlated within the Hückel framework using the Finnegan-Streitwieser model. INDO calculations were also carried out on these molecules and the results are discussed.

Mills and Nixon advanced the first theoretical discussion of the reduced reactivity of the  $\alpha$  position of strained benzocycloalkenes in 1930.<sup>5</sup> At present, the origin of this effect is still not clear. Markgraf, *et al.*, have reported that the basicity of the nonbonding electrons of a nitrogen  $\alpha$  to a fused, strained ring decreases as the strain in the ring increases.<sup>6</sup> The acidity of protons  $\alpha$  to a strained ring has been reported to increase as strain increases.<sup>7,8</sup> Several papers have appeared reporting marked changes in relative reactivities of various positions in a series of hydrocarbons toward electrophilic substitution as ring strain is introduced.<sup>9-13</sup> Also, uv and charge-transfer spectra<sup>14</sup> and proton nmr data<sup>15</sup> on benzocycloalkenes have been reported.

Several arguments have been presented to explain these observations.<sup>7-10</sup> The explanation presented by Finnegan<sup>7</sup> and Streitwieser<sup>8</sup> is the only one that accounts for the changes in both chemical and physical properties. In this model, the ring junction carbon atoms containing the fused, strained ring are rehybridized to accommodate the small bond angles. The  $\sigma$  bonds in the strained ring have increased p character and the remaining  $\sigma$  bonds to the carbons  $\alpha$  to the strained ring have more s character. This increase in s character results in an increase in orbital electronegativity which results in a polarization of electrons away from the  $\alpha$  carbon atoms. This would account for the reduced reactivity of the  $\alpha$  position toward electrophiles and the increase in acidity of the  $\alpha$  proton. Further, the reduced basicity of the nitrogen lone pair is accounted for when the  $\alpha$  atom is a nitrogen atom.

We have demonstrated that the Finnegan-Streitwieser model can also be used to explain the changes in half-wave reduction potentials<sup>1,16</sup> and the changes in spin densities of aromatic radical anions<sup>1,17,18</sup> that we have observed. We have been able to correlate this data within the Hückel framework by making the  $\alpha$  carbons more electronegative with increased strain and the ring juncture carbons more electropositive. Finally, one of the authors has recently reported the use of simple perturbation theory within the Hückel framework plus the parameters derived from our

Chart I  
Compounds under Investigation<sup>a</sup>



<sup>a</sup> Numbering system used for discussion and hfsc assignment.

esr and polarographic studies to explain the observed decrease in reactivity of the  $\alpha$  position of benzocyclobutene.<sup>19</sup>

In this paper, we report the results of an esr study of the radical anions of a series of naphthalene hydrocarbons having varying degrees of ring strain. The following compounds, shown in Chart I, were investigated: 2,3-dimethylnaphthalene (I), naphtho[*b*]cyclobutene (II), 5,6-benzindan (III), and 1,2,3,4-tetrahydroanthracene (IV). The changes in spin densities observed can again be explained by the Finnegan-Streitwieser model and can be correlated within the Hückel framework using parameters derived from our previous studies.<sup>1,16,17</sup>

### Experimental Section

Usual high-vacuum techniques using alkali metals and ethereal solvents were employed to prepare the radical anions studied. The initial hydrocarbon concentration was approximately  $5 \times 10^{-3}$  M. Dimethoxyethane (Aldrich), tetrahydrofuran (MCB), and diethyl ether (Allied) were dried by several distillations from lithium aluminum hydride (Alfa), degassed on the vacuum line using the freeze-pump-thaw technique, and distilled under vacuum to solvent bumpers containing sodium-potassium alloy (Unified Science Associates). Hexamethylphosphoramide (Aldrich) was dried by