

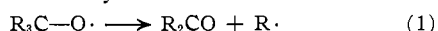
## ORGANIC AND BIOLOGICAL CHEMISTRY

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY, NEW YORK 27, N. Y.]

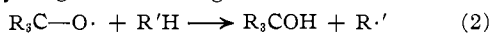
Positive Halogen Compounds. VI. Effects of Structure and Medium on the  $\beta$ -Scission of Alkoxy Radicals<sup>1</sup>BY CHEVES WALLING AND ALBERT PADWA<sup>2</sup>

RECEIVED DECEMBER 29, 1962

The effect of structure on the rate of  $\beta$ -scission of alkoxy radicals has been investigated by carrying out the photodecomposition of a series of *t*-alkyl hypochlorites and determining the relative yields of products of  $\beta$ -scission and attack on cyclohexane. Results show increasing  $\beta$ -scission in the order methyl < chloromethyl < ethyl, benzyl < isopropyl < *t*-butyl. Activation energy differences parallel resonance stabilization of the resulting radicals, but the rate for benzyl scission appears anomalous because of a small *PZ* factor for the reaction. The opening of a cyclopentane ring by  $\beta$ -scission is shown to occur 10–15 times as readily as that of a cyclohexane ring. In the presence of olefins,  $\beta$ -scission of the benzyldimethylmethoxy radical becomes its sole reaction, a result interpreted as a solvent effect. It is pointed out that solvent effects on competitive radical reactions must arise primarily from solvation of *transition states*, and it is suggested that, while such solvation is possible for unimolecular radical reactions, steric factors may often prevent transition state solvation in bimolecular reactions.

The  $\beta$ -scission of alkoxy radicals

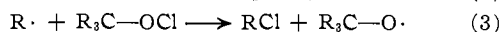
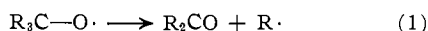
is a well established process which competes with their attack on hydrogen-containing substrates



Discussion of the reaction and early references are given by Walling<sup>3</sup> and, in more detail, by Gray and Williams.<sup>4</sup> For the case of  $R = CH_3$  (the *t*-butoxy radical) Gray and Williams estimate  $\Delta H = 5$  kcal./mole,  $E_a = 13$  kcal./mole for the scission process. This value of  $\Delta H$  may be compared with the corresponding value for  $\beta$ -scission of an alkyl radical, approximately 20 kcal./mole.<sup>5</sup> As a consequence of this higher value,  $\beta$ -scission of alkyl radicals is significant only at high temperatures as in hydrocarbon pyrolyses.<sup>6</sup>

*A priori* one would anticipate that the energetics for  $\beta$ -scission would become more favorable, and the rate of reaction 1 would increase, with increasing resonance stabilization of the resulting radical  $R\cdot$  in the order  $R =$  methyl < primary alkyl < secondary < tertiary. Gray and Williams<sup>4</sup> discuss evidence supporting this deduction, and, since the work described here was begun, additional examples have been reported<sup>7–10</sup> consistent with the sequence given.

The photoinduced reactions of *t*-alkyl hypochlorites provide a very convenient means of studying alkoxy radical reactions, since alkoxy radicals are chain carriers both in hypochlorite decompositions involving the sequence<sup>11</sup>



(1) Taken from the Ph.D. thesis of Albert Padwa, Columbia University, 1962. Support of this work by the National Science Foundation is gratefully acknowledged.

(2) University Fellow, 1961–1962.

(3) C. Walling, "Free Radicals in Solution," John Wiley & Sons Inc., New York, N. Y., 1957, pp. 470–473.

(4) P. Gray and A. Williams, *Chem. Rev.*, **59**, 239 (1959).

(5) Cf. ref. 3, pp. 212.  $\beta$ -Scission is, of course, the reverse of radical addition to a double bond.

(6) This difference also provides the basic explanation of the fact that, while olefins readily polymerize, linear polyacetals are in general unstable in respect to the corresponding carbonyl compounds even at room temperature; cf. J. B. Conant and W. R. Peterson, *J. Am. Chem. Soc.*, **54**, 628 (1932).

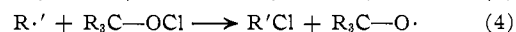
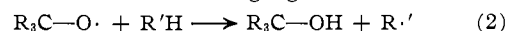
(7) F. D. Greene, *ibid.*, **81**, 2688 (1959); F. D. Greene, M. L. Savitz, H. H. Lau, F. D. Osterholtz and W. N. Smith, *ibid.*, **83**, 2197 (1961); F. D. Greene, M. L. Savitz, H. H. Lau, F. D. Osterholtz, W. N. Smith and P. M. Zanet, *J. Org. Chem.*, **28**, 55 (1963).

(8) J. K. Kochi, *J. Am. Chem. Soc.*, **84**, 1193 (1962).

(9) P. Kabasakalian and E. R. Townley, *ibid.*, **84**, 2723 (1962).

(10) C. Walling and A. Padwa, *ibid.*, **84**, 2854 (1962). This paper is a preliminary report of the work described here.

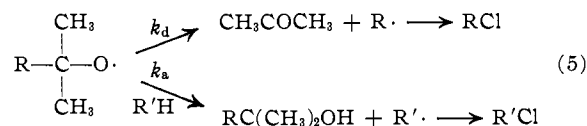
(11) A. D. Yoffe, *Chem. Ind.* (London), 963 (1954).

and in their use as chlorinating agents<sup>12</sup> *via* the chain

Since the chlorination sequence (and, in some cases the decomposition) proceeds readily at temperatures as low as  $-78^\circ$ , the competition between  $\beta$ -scission and hydrogen abstraction (or in unsymmetric hypochlorites,  $R_1R_2R_3COCl$ , the direction of  $\beta$ -scission) can be studied conveniently in solution over a very wide temperature range. Such an investigation is the subject of this paper.

## Results and Discussion

From what has been said previously, photolysis of a hypochlorite of the structure  $RC(CH_3)_2OCl$  in the presence of a large excess of a reactive hydrocarbon  $R'H$  will yield alkyl chloride  $RCl$  plus acetone<sup>13</sup> and alcohol  $RC(CH_3)_2OH$ , plus chlorinated hydrocarbon  $R'Cl$  in amounts depending upon the relative rates of hydrogen abstraction and  $\beta$ -scission of the alkoxy radical involved



The ratio of rate constants  $k_d/k_a$  in such a system is given by

$$\frac{k_d}{k_a} = [\text{R}'\text{H}] \frac{[\text{RCl}] \text{ (or } [\text{CH}_3\text{COCH}_3] \text{) formed}}{[\text{RC}(\text{CH}_3)_2\text{OH}] \text{ (or } [\text{R}'\text{Cl}] \text{) formed}} \quad (6)$$

Further, if the assumption is made that  $k_a$ 's are essentially independent of the alkoxy radical, comparisons of the  $k_d/k_a$  ratios obtained will give the relative rates of the  $\beta$ -scissions involved. Such an assumption is plausible, since  $D$  (RO-H) (and accordingly the energetics of hydrogen abstraction) is within experimental uncertainty independent of  $R$ ,<sup>4</sup> and its validity is examined further below.

Results of a series of such experimental measurements using cyclohexane as the hydrocarbon are shown in Table I. The value for  $R = CH_3$  is taken from another investigation,<sup>14</sup> carried out at much lower hydrocarbon concentration and a somewhat different technique, which will be described elsewhere.

Table I clearly substantiates the cleavage sequence methyl < ethyl < isopropyl < *t*-butyl, both in rate and decreasing activation energy. The large difference

(12) C. Walling and B. B. Jacknow, *J. Am. Chem. Soc.*, **82**, 6108 (1960).

(13) Except for certain cases which will be mentioned, only traces of  $RCOCH_3$  and  $CH_3Cl$  are produced in these reactions.

(14) C. Walling and P. Wagner, unpublished work.

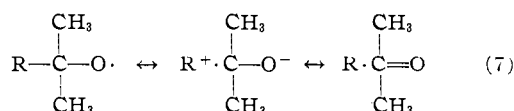
TABLE I  
DECOMPOSITION OF 0.56 M RC(CH<sub>3</sub>)<sub>2</sub>OCl IN CCl<sub>4</sub> IN PRESENCE  
OF CYCLOHEXANE (R'H)

R	T, °C.	[R'H]	k <sub>d</sub> /k <sub>a</sub> <sup>f</sup>	E <sub>d</sub> - E <sub>a</sub> <sup>d</sup>	(PZ) <sub>d</sub> /(PZ) <sub>a</sub> <sup>e</sup> (× 10 <sup>-2</sup> )
CH <sub>3</sub>	0	a	0.002		
	40	a	.021	10.0	500
	70	a	.082		
CH <sub>2</sub> Cl	0	1.55	.051		
	40		.121	4.6	0.13
	70		.268		
C <sub>6</sub> H <sub>5</sub>	0	1.55	.242		
	40		.477	5.1	1.72
	70		1.00		
C <sub>2</sub> H <sub>5</sub>	0	1.55	1.14		
	40		2.09	3.3	0.42
	70		3.36		
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub>	0	1.55	1.80		
	40		1.98	0.7	0.006
	70		2.28		
<i>i</i> -C <sub>3</sub> H <sub>7</sub>	0	4.65	61.5		
	40		76.4	1.7	1.15
	70		109		
<i>t</i> -C <sub>4</sub> H <sub>9</sub>	0	7.75	>300 <sup>b</sup>		
	40		>300	...	...
	70		>300		
(CH <sub>2</sub> ) <sub>4</sub> <sup>c</sup>	0	5.7	97		
	80		148	1.1	7.0
(CH <sub>2</sub> ) <sub>6</sub> <sup>c</sup>	0	5.7	6.6		
	80		15.5	2.1	3.1

<sup>a</sup> See text for explanation (value at 0° is extrapolated). <sup>b</sup> A minimum value, only cleavage products detected. <sup>c</sup> 1-Methylcyclopentyl and 1-methylcyclohexyl hypochlorites (1.0 M). <sup>d</sup> Difference in activation energies for decomposition and abstraction (kcal./mole). <sup>e</sup> Ratio of PZ factors for decomposition and abstraction. <sup>f</sup> Determined from ratio of acetone or alkyl chloride to alcohol or cyclohexyl chloride depending upon suitability of G.L.C. analysis. Experimental error is estimated as approximately 5%.

between methyl and ethyl compared with the other members of the series is probably ascribable to the fact that β-scission to yield a methyl radical is endothermic by 5 kcal., while, below ethyl, resonance stabilization of the resulting radicals probably makes the cleavages exothermic. As a result, over-all energy differences have a smaller effect on the energies of the transition states involved. The difference between CH<sub>3</sub> and the other alkyl groups would be even larger were it not for a more favorable PZ factor difference for the methyl radical case.

While the sequence is certainly consistent with over-all energetics and resonance stabilization of the radicals produced, other factors may be involved as well. Relief of steric strain by the expulsion of increasingly bulky groups would be expected to yield the observed order, as would the contribution of possible charge-transfer structures to transition states



The center structure in 7 appears plausible since the incipient carbonyl group has the electronic structure of a ketyl. The importance of such a polar effect might account for the considerably lower amount of β-scission observed for CH<sub>2</sub>Cl compared with C<sub>2</sub>H<sub>5</sub>, since the resulting radicals should have comparable stability.<sup>15</sup> Results on the system for R = benzyl are also anomalous in that, while the activation energy is the lowest observed, as would be expected from the high resonance stabilization of the benzyl radical produced, the rate is

(15) Cf. ref. 3, p. 50.

comparable to R = ethyl apparently because of a small PZ factor. Conceivably here the transition state is restricted to only a small range of conformations to permit delocalization of the incipient radical.

The remaining examples also require special mention. The case of R = C<sub>6</sub>H<sub>5</sub> is unique in that methyl rather than phenyl is lost, yielding acetophenone and methyl chloride. While this direction of cleavage is well known from investigations of the decomposition of cumyl peroxides,<sup>16</sup> we here see that the loss of methyl is apparently accelerated many fold over that observed with the *t*-butoxy radical. A plausible source of the additional driving force would be enhanced stability of acetophenone compared to acetone due to overlap between the orbitals of the carbonyl group and the benzene ring.

Finally, turning to the cyclic systems at the bottom of the table, we see that opening of the essentially unstrained cyclohexane ring occurs only a little more readily than the loss of an ethyl group. The cyclopentyl ring with an estimated ring-strain of 6.5 kcal./mole<sup>17</sup> opens more readily. This reaction, incidentally, was first described by Cairns and Englund,<sup>18</sup> as an elegant route to ω-chloroketones. For this purpose, of course, it is desirable to run the decomposition in an inert solvent, and preferably at high dilution and a high temperature. While 1-methylcyclopentyl hypochlorite (1.9 M) in CCl<sub>4</sub> at 0° gives a 97% yield of ω-chloroacetone, the yield from 1-methylcyclohexyl hypochlorite is only 74% under the same conditions. At 80° and 0.001 M concentration it increases to 97%.

Our conclusions on the relative rates of β-scission processes can be checked by investigating the products obtained from decomposition of suitable unsymmetric hypochlorites, R<sub>1</sub>R<sub>2</sub>R<sub>3</sub>COCl. Chloromethyl dimethylcarbinyl hypochlorite yields significant quantities of both acetone plus methylene dichloride and chloroacetone plus methyl chloride, and we have obtained further data on the decomposition of methylethylisopropylcarbinyl and methylethylbenzylcarbinyl hypochlorite. Results of such "direct" competitions are compared in Table II with "indirect" measurements (from Table I). While results are in qualitative agreement, they differ significantly, presumably either because our assumption of the constancy of k<sub>a</sub> is not entirely valid, or because steric interactions between groups slightly alter values of k<sub>d</sub>.

TABLE II  
"DIRECT" AND "INDIRECT" MEASUREMENT OF RELATIVE RATES  
OF β-SCISSION

T, °C.	Isopropyl:ethyl		Benzyl:ethyl		Chloromethyl: methyl	
	Direct	Indirect	Direct	Indirect	Direct	Indirect
0	39.3	53.9	2.84	1.58	40	26
40	27.1	36.4	2.72	0.95		
70	21.5	32.5	2.68	0.68	30	3
ΔE <sub>a</sub> <sup>a</sup>	1.65	1.5	0.2	2.2	1.0	5.4

<sup>a</sup> Activation energy differences in kcal./mole.

**Decomposition of *t*-Butyl Hypochlorite in CCl<sub>4</sub>.**—Although *t*-butyl hypochlorite is reported to decompose quite smoothly to acetone and methyl chloride in the gas phase,<sup>11</sup> and most of the compounds of Table I give alkyl chloride and acetone in good yield on irradiation in CCl<sub>4</sub> even at 0°, the decomposition of *t*-butyl hypochlorite in CCl<sub>4</sub> is much slower (requiring 8–10 hr. under conditions where other *t*-hypochlorites are con-

(16) M. S. Kharasch, A. Fono and W. Nudenberg, *J. Org. Chem.*, **15**, 748 (1950).

(17) S. W. Benson, *J. Chem. Phys.*, **34**, 521 (1961).

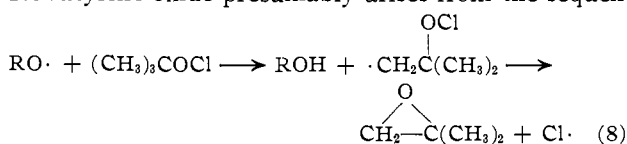
(18) T. L. Cairns and B. E. Englund, *J. Org. Chem.*, **21**, 140 (1956); cf. also J. W. Wilt and J. W. Hill, *ibid.*, **26**, 3523 (1961).

sumed in 10–30 min.) and, since the slowness of the  $\beta$ -scission process permits a number of other reactions to compete, yields a complex mixture of products (rather similar results have been noted in chlorobenzene<sup>12</sup>). Analysis by gas-liquid chromatography (G.L.C.) reveals at least 9 peaks, identified (in their order of elution) as methyl chloride, methylene chloride, acetone, isobutylene oxide, *t*-butyl alcohol, chloroacetone, dichloroacetone, 1-chloro-2-methyl-2-propanol and a dichloroalcohol. Approximate yields of the major products as a function of hypochlorite concentration and temperature are listed in Table III.

TABLE III  
PRODUCTS OF DECOMPOSITION OF *t*-BUTYL HYPOCHLORITE IN CCl<sub>4</sub>

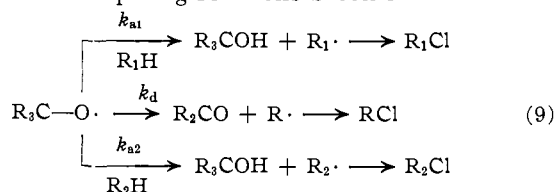
[ROCl] <sub>0</sub>	0°			80°		
	0.46	2.1	8.4	0.46	2.1	8.4
Products, mole %						
Acetone	22	17	13	55	50	33
<i>t</i> -Butyl alcohol	50	62	58	21	27	46
Isobutylene oxide	5	2.6	0.36	4.4	2.6	Trace
Chloroacetone	4	3	2	15	11	10
1-Chloro-2-methyl-2-propanol	21	22	24	11	15	16

Acetone and methyl chloride (not measured quantitatively) must arise from  $\beta$ -scission, and yields, as expected, increase both with temperature and dilution. The *t*-butyl alcohol comes from *t*-butoxy radical attack both on hypochlorite and its decomposition products, and yields rise as those of acetone decrease. The 1-chloro-2-methyl-2-propanol may come from chlorination of either hypochlorite or *t*-butyl alcohol, but the chloroacetone must come chiefly from chlorination of acetone, since chlorinated hypochlorite, on conversion to chloro-*t*-butoxy radicals, cleaves chiefly to acetone (Table I). In any case, the fact that a smaller fraction of acetone than of alcohol has been chlorinated emphasizes the deactivating effect of carbonyl groups toward alkoxy radical attack on neighboring hydrogens.<sup>12</sup> Isobutylene oxide presumably arises from the sequence



analogous to its postulated path of formation in the decomposition of *t*-butyl peroxide.<sup>19</sup> If so, the increase in yield with dilution is expected, since dilution increases the life of the intermediate radical. The higher yield relative to chloroalcohol at 80° suggests that 8 has a higher activation energy than attack of the intermediate radical on hypochlorite.

**Hypochlorite Decompositions in the Presence of Olefins.**—In most of the previous discussion we have considered the effect of changing alkoxy radical structure upon the ratio of rate constants  $k_d/k_a$  for attack upon a single substrate (cyclohexane) and have interpreted the variations in the ratio as arising primarily from changes in  $k_d$ . Alternatively,  $k_d$  may be fixed and  $k_a$  varied by allowing a single hypochlorite to react with a series of substrates. Thus, for a pair of substrates the competing reactions become



(19) E. R. Bell, F. F. Rust and W. E. Vaughan, *J. Am. Chem. Soc.*, **72**, 337 (1950).

The ratio  $k_{a1}/k_{a2}$  may now be determined either *directly* in a single experiment by measuring the relative rates of disappearance of R<sub>1</sub>H and R<sub>2</sub>H, or *indirectly* by treating the hypochlorite with R<sub>1</sub>H and R<sub>2</sub>H separately and then comparing  $k_d/k_{a1}$  with  $k_d/k_{a2}$ . This technique was first employed by Raley, Rust and Vaughan<sup>20</sup> in the study of *t*-butoxy radicals from di-*t*-butyl peroxide, and has been used extensively since, although we shall here show that it is subject to serious suspicion.

We elected to carry out a series of such measurements, with R<sub>1</sub>H = cyclohexane and R<sub>2</sub>H = cyclohexene, chosen in the expectation that its greater reactivity would yield alcohol:acetone ratios more amenable to accurate measurement. The quite unexpected results are shown in Table IV.

TABLE IV  
DECOMPOSITION OF HYPOCHLORITES RC(CH<sub>3</sub>)<sub>2</sub>OCl IN THE PRESENCE OF CYCLOHEXANE (R<sub>1</sub>H) AND CYCLOHEXENE (R<sub>2</sub>H)

R	[R <sub>1</sub> H]	[R <sub>2</sub> H]	$k_d/k_{a1}^a$	$k_d/k_{a2}$	$k_{a2}/k_{a1}$	
					Direct	Indirect
CH <sub>3</sub>	...	...	0.021	...	8.46 ± 0.74 <sup>b</sup>	...
CH <sub>2</sub> Cl	1.55	...	.121	...	7.63 ± .47	...
C <sub>6</sub> H <sub>5</sub>	1.55	...	.477	...	8.84 ± .63	...
C <sub>2</sub> H <sub>5</sub>	1.55	...	2.09	...	7.54 ± .54	3.94 ± 0.20
<i>i</i> -C <sub>3</sub> H <sub>7</sub>	...	1.64	...	0.532	...	...
	4.65	...	76.4	...	...	1.12 ± 0.09
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub>	...	4.93	...	68.0	...	...
	1.55	...	1.98	...	...	<0.03
		1.64	...	>70	...	...

<sup>a</sup> From Table I. <sup>b</sup> From C. Walling and W. Thaler, *J. Am. Chem. Soc.*, **83**, 3877 (1961).

From the table it is evident that *direct* measurement of  $k_{a2}/k_{a1}$  gives sensibly the same value for four alkoxy radicals, but that *indirect* measurement gives very different values. Further, in the one case where both techniques can be applied with precision they are not in agreement. The most remarkable result of indirect measurement occurs in the case of benzyldimethylcarbinyl hypochlorite (R = benzyl) where only cleavage products (benzyl chloride and acetone) were detected in cyclohexene solution. In an attempt to see whether this could be the consequence of a decrease in  $k_{a2}$ , we also investigated the direct competition of cyclohexene and cyclohexane toward this hypochlorite.

In the presence of as little as 3.6 mole % cyclohexene in the hydrocarbon mixture, only cleavage products resulted, no hydrocarbon was chlorinated, and the cyclohexene was recovered unchanged. Similar results were observed with a number of other olefins, Table V. Only those with strong electron-withdrawing groups, acrylonitrile and methyl acrylate, gave traces of alcohol, although aromatic solvents, at this level, have no comparable effect.<sup>21</sup>

Cleavage was also the sole reaction when attempts were made to chlorinate other hydrocarbons in the presence of small quantities of cyclohexene or cyclopentene, Table VI. We also see that relative reactivities calculated *indirectly* in the absence of olefin are not in very good agreement with those obtained with *t*-butyl hypochlorite, 1:1.58:0.64:0.71 for toluene:ethylbenzene:2,3-dimethylbutane:cyclohexane for the indirect measurement compared with 1:2.30:3.15:6.00 for the direct comparison.<sup>12</sup>

From our results, olefins are seen to exert a marked influence upon the reactive properties of alkoxy radi-

(20) J. H. Raley, F. F. Rust and W. E. Vaughan, *ibid.*, **70**, 1336 (1948).

(21) Small effects of aromatic solvents at high concentrations on the properties of *t*-butoxy radicals have been reported, both on selectivity<sup>12</sup> and on the acetone:alcohol ratios produced in the presence of reactive substrates; G. A. Russell, *J. Org. Chem.*, **24**, 300 (1959). We are now investigating the latter, and find the solvent effect can be quite large.<sup>14</sup>

TABLE V

EFFECT OF OLEFINS ON THE DECOMPOSITION OF BENZYLDIMETHYL-CARBINYL HYPOCHLORITE (0.56 M)

Solvent, C<sub>2</sub>F<sub>3</sub>Cl<sub>3</sub> plus 1.55 M cyclohexane, 40°

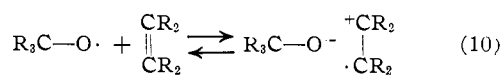
Olefin, M	[Acetone]/[Alcohol]
None	1.28 ± 0.07
Cyclohexene, 0.055	>40
Cyclopentene, 0.097	>40
Pentene-1, 0.104	>40
Hexene-2, 0.067	>40
Heptene-2, 0.120	>40
Octene-1, 0.055	>40
4-Methylpentene-2, 0.091	>40
Acrylonitrile, 0.130	20
Methyl acrylate, 0.091	27
Methyl methacrylate, 0.082	>40
Anisole, 0.078	1.34
Benzene, 0.097	1.36
Chlorobenzene, 0.042	1.30
<i>o</i> -Dichlorobenzene, 0.074	1.24
Nitrobenzene, 0.082	1.28

TABLE VI

EFFECT OF OLEFINS ON FURTHER HYDROCARBON CHLORINATIONS BY BENZYLDIMETHYL-CARBINYL HYPOCHLORITE (0.56 M) in C<sub>2</sub>F<sub>3</sub>Cl<sub>3</sub>, 40°

Hydrocarbon, M	Olefin, M	[Acetone]/[Alcohol]
Cyclopentane, 1.79	...	1.41
	Cyclohexene, 0.064	>40
2,3-Dimethylbutane, 1.52	Cyclopentene, 0.072	>40
	...	1.40
Toluene, 1.87	Cyclohexene, 0.051	>40
	Cyclopentene, 0.066	>40
Ethylbenzene	...	0.73
	Cyclohexene, 0.104	>40
Ethylbenzene	Cyclopentene, 0.089	>40
	...	0.52
Ethylbenzene	Cyclohexene, 0.088	>40
	Cyclopentene, 0.069	>40

cals (particularly the benzyl dimethylmethoxy radical), without themselves appearing in the reaction products, the sort of phenomenon which is commonly described as a solvent effect. By analogy to the current picture of solvent effects in chlorine atom reactions,<sup>22,23</sup> such interaction might be of the charge transfer type



plausible since, in both cases, the odd electron exists on a strongly electronegative atom.

Two phenomena, however, need to be explained: First, why does solvent interaction favor  $\beta$ -scission of the alkoxy radical (the process of higher activation energy) without affecting significantly the selectivity of hydrogen abstraction processes? Second, why is the effect particularly marked with the benzyl dimethylmethoxy radical?

In considering the first question, we will first assume that association of alkoxy radicals with solvent is a rapid reversible process, so that all reactions proceed from a starting material which is essentially the equilibrium mixture of complexed and uncomplexed radicals. Under such conditions, the effect of solvent on the relative rates of competing reactions of the alkoxy radicals will be determined solely by solvation effects on the transition states involved. Solvent interaction with the transition state for  $\beta$ -scission presents no diffi-

culties, but in the transition state involving an alkoxy radical and a substrate such as cyclohexene, solvent molecules should be sterically excluded from close vicinity to the alkoxy radical. Accordingly, the  $\beta$ -scission process is favored. No such difficulty should arise with halogen atom reactions since the "back side" of a complexed halogen atom is presumably still available to attack a C-H bond. This conclusion, that the solvation of transition states for radical-substrate processes presents serious steric difficulties which are not present for unimolecular reactions ( $\beta$ -scission and rearrangements) seems to have been generally overlooked, and may account for the paucity of examples of solvent effects in radical-substrate reactions. It also suggests that the place to look for solvent effects is in the competition between unimolecular reactions of radicals and their bimolecular attack on substrates rather than in the competitions between bimolecular processes which have usually been examined heretofore.

The second question, why the solvent effect is particularly large with the benzyl dimethylmethoxy radical, is harder to answer definitely. Using the variation in the "indirect" value of  $k_{a2}/k_{a1}$  as a measure of solvent effect, we see from Tables I and IV that it increases regularly as ( $E_d - E_a$ ) grows smaller. This result might be interpreted in terms of "Hammond's postulate."<sup>24</sup> As the activation energy for  $\beta$ -scission decreases, the transition state resembles more the "solvatable" alkoxy radical, rather than the product ketone. Alternatively, as the activation energy for  $\beta$ -scission decreases, our assumption about equilibrium between complexed and uncomplexed radicals may be in error, and the rate of  $\beta$ -scission of a complexed radical may become actually faster than its rate of dissociation.<sup>25</sup>

## Experimental

**Materials.**—Unless indicated, solvent, hydrocarbons and alcohols used for the preparation of hypochlorites were commercial materials, distilled and dried (if necessary) before use. Physical constants were determined and the absence of impurities was checked by G.L.C. analysis. Carbon tetrachloride was purified by washing with aqueous alcoholic KOH, H<sub>2</sub>SO<sub>4</sub>, and water, dried and fractionated through an 8-plate column. Alcohols which were not commercially available were synthesized from appropriate Grignard reagents and ketones by essentially standard methods, thus: phenyl dimethylcarbinol from bromobenzene and acetone; yield 73%, b.p. 93–94° (13 mm.),  $n_D^{25}$  1.5207; *t*-butyl dimethylcarbinol from methyl *t*-butyl ketone and methyl iodide; yield 66%, b.p. 71–72° (84 mm.),  $n_D^{25}$  1.4265; methylethylisopropylcarbinol from methyl isopropyl ketone and ethyl bromide; yield 58%, b.p. 83–83.5° (104 mm.),  $n_D^{25}$  1.4272; methylethylbenzylcarbinol from methyl benzyl ketone and ethyl bromide; yield 72%, b.p. 96–97° (3.5 mm.),  $n_D^{25}$  1.5132; 1-methylcyclohexanol from cyclohexanone and methyl iodide; yield 61%, b.p. 165–166°,  $n_D^{25}$  1.4567; 1-methylcyclopentanol from cyclopentanone and methyl iodide; yield 65%, b.p. 136–137°,  $n_D^{25}$  1.4423.

**Preparation of Hypochlorites.**—*t*-Butyl hypochlorite was synthesized by the method of Teeter and Bell.<sup>26</sup> Since this technique, using NaOH, Cl<sub>2</sub> and the alcohol, was sometimes found to yield highly chlorinated by-products with higher alcohols, the remaining hypochlorites were prepared from hypochlorous acid and the alcohol essentially as described by Anbar and Dostrovsky.<sup>27</sup> Eighty ml. of a 1 M solution of the alcohol in CCl<sub>4</sub> or Freon 113 (C<sub>2</sub>F<sub>3</sub>Cl<sub>3</sub>) was placed in a stirred round-bottom flask and cooled to 0°. Two hundred ml. of 0.8 M hypochlorous acid<sup>28</sup> was added and the mixture stirred 2–3 hr. in the dark. The non-aqueous layer containing the hypochlorite was separated, washed with 20 ml. of 5% Na<sub>2</sub>CO<sub>3</sub>, twice with water, and dried over Na<sub>2</sub>SO<sub>4</sub>. The hypochlorite concentration was determined by iodometric titration, and the solution was used as such without further isolation, since solutions showed no –OH absorption in the infrared, indicating quantitative conversion.

(24) G. S. Hammond, *ibid.*, **77**, 334 (1955).

(25) Failure of this equilibrium assumption would not vitiate our previous argument concerning the importance of steric effects on transition state solvation, but would simply make the rate of complex formation rate determining for the  $\beta$ -scission.

(26) H. M. Teeter and E. W. Bell, *Org. Syntheses*, **32**, 20 (1952).

(27) M. Anbar and I. Dostrovsky, *J. Chem. Soc.*, 1105 (1954).

(28) G. H. Cady, *Inorg. Syntheses*, **5**, 156 (1957).

(22) G. A. Russell, *J. Am. Chem. Soc.*, **79**, 2977 (1957); **80**, 4987 (1958).

(23) C. Walling and M. F. Mayahi, *ibid.*, **81**, 1485 (1959).

Reactions were carried out in sealed degassed tubes, placed in thermostats and irradiated by incandescent lamps essentially as in previous work.<sup>12</sup>

Analyses of reaction mixtures were carried out by G.L.C. techniques using either a Perkin-Elmer model 154 or, more frequently, an Aerograph A-350 instrument. Two columns were used with the Perkin-Elmer instrument, A (diisodecyl phthalate) and C (dimethyl siloxane polymer); and five with the Aerograph, Carbowax 20 M (polyethylene oxide), "DEGS" (diethylene glycol polysuccinate), "Craig" (butanediol polysuccinate), didecyl phthalate and silicone (GE SF 96) all on firebrick. Products from each hypochlorite were collected and identified (by infrared spectra, index of refraction and boiling point) as described below. In quantitative experiments to determine relative amounts of  $\beta$ -scission and attack on cyclohexane (Table I) peak areas for acetone (or alkyl chloride) were compared with peak areas for alcohol (or cyclohexyl chloride) and results converted to molar ratios by calibration of the instrument with known mixtures. Relative reactivities of hydrocarbons were determined by hydrocarbon disappearance (or appearance of chlorinated products) using internal standards as previously.<sup>12</sup> Experiments were run in triplicate and analyzed in duplicate. Reproducibility was 2-6%, and results are reported as the mean, with experimental error the deviation from the mean.

*t*-Butyl Hypochlorite.—Products of decomposition in  $\text{CCl}_4$  were analyzed on the A column at 55 and 115°. Acetone, *t*-butyl alcohol, chloroacetone and 1-chloro-2-methyl-2-propanol were collected and identified. Methylene chloride and isobutylene oxide, present in very small quantities, were identified only by retention time. Peaks identified as dichloroacetone and dichloroalcohol had the same retention times as products obtained by *t*-butyl hypochlorite chlorination of chloroacetone and 1-chloro-2-methyl-2-propanol, respectively.

*t*-Amyl Hypochlorite.—Ethyl chloride, acetone, *t*-amyl alcohol and chloroacetone were collected (A column, 64°) and identified by comparison with authentic samples.

Chloromethylmethylcarbinyl Hypochlorite.—Methylene chloride, acetone, chloroacetone and 1-chloro-2-methyl-2-propanol were collected (C column, 115°) and identified.

Phenylmethylcarbinyl Hypochlorite.—Acetophenone was collected and identified. Acetone, chlorobenzene (traces) and phenylmethylcarbinol were identified by retention times (Craig and Carbowax columns).

Isopropylmethylcarbinyl Hypochlorite.—Isopropyl chloride, acetone and the carbinol were separated (dinonyl phthalate column, programmed 60-150°), collected and identified.

*t*-Butylmethylcarbinyl Hypochlorite.—Acetone and *t*-butyl chloride were separated and identified (DEGS column, programmed 60-130°). No more than traces of carbinol were detected.

Benzylmethylcarbinyl Hypochlorite.—Acetone, benzyl chloride and the carbinol were collected and identified (dinonyl phthalate column programmed 60-160°). In the presence of cyclohexene, no carbinol was detected. In the hydrocarbon chlorinations (Tables IV-VI) chlorination products of cyclohexane, cyclopentane, toluene, ethylbenzene and 2,3-dimethylbutane were all collected and identified.

Methylethylisopropylcarbinyl Hypochlorite.—Ethyl chloride, isopropyl chloride, methyl isopropyl ketone and methyl ethyl ketone were all collected and identified (silicone column, programmed 60-180°).

Methylethylbenzylcarbinyl Hypochlorite.—Ethyl chloride, benzyl chloride, methyl ethyl ketone and methyl benzyl ketone were all collected and identified (Craig column, programmed 174-240°).

1-Methylcyclopentyl Hypochlorite.—Products were separated on a Carbowax column, programmed at 60-210°. The 6-chloro-2-hexanone was identified as its 2,4-dinitrophenylhydrazone, m.p. 81-82°.

1-Methylcyclohexyl Hypochlorite.—Products were separated as in the previous case. The 7-chloro-2-heptanone was identified as its 2,4-dinitrophenylhydrazone, m.p. 95-96°.

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## Positive Halogen Compounds. VII. Intramolecular Chlorinations with Long Chain Hypochlorites<sup>1</sup>

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The light induced radical chain decomposition of *t*-hypochlorites with side chains of three carbons or longer has been shown to occur largely via an intramolecular path (1,5-shift of hydrogen) to give  $\delta$ -chloroalcohols in yields of 15-80% plus in some cases small quantities of  $\epsilon$ -chloroalcohols. The competition with  $\beta$ -scission of the intermediate alkoxy radicals is concentration independent, and the intramolecular reaction is important even in reactive hydrocarbon solvents. Reactivity of  $\delta$ -hydrogens lies in the order  $1^\circ < 2^\circ < 3^\circ$ , 1:9:47, paralleling intermolecular reactions of alkoxy radicals. With suitable precautions,  $\delta$ -chloroalcohols can be obtained similarly from primary and secondary hypochlorites, and base catalyzed cyclization provides a convenient synthesis of a variety of tetrahydrofurans.

An intramolecular radical reaction involving hydrogen transfer was apparently first noted by Grob and Kammuler in 1937, who reported a 5% yield of 5,6-diphenyldecane from the decomposition of  $\epsilon$ -phenylcaproyl peroxide.<sup>3</sup> Hydrogen transfer was suggested as an explanation of free radical isomerization by Kossiakoff and Rice in 1943,<sup>4</sup> and has subsequently been recognized as a factor in chain branching during ethylene polymerization,<sup>5</sup> and as the source of certain products of autoxidation processes.<sup>6,7</sup> Wawzonek<sup>8</sup> and, in more detail, Corey<sup>9</sup> have shown that such transfer is a key step in the Hofmann-Löffler-Freitag reaction (conversion of *N*-chloroamines to pyrrolidines), and numerous additional examples are recognized. In con-

trast to the behavior of carbonium ions, free radicals do not appear to undergo ready 1,2-migration of hydrogen.<sup>10</sup> Rather, reaction occurs preferentially through quasi-6-membered transition states to give 1,5-hydrogen transfers. Barton has pointed out the synthetic possibilities of such 1,5-hydrogen transfers, and has used them most effectively in the steroid series by photolyzing appropriate nitrite esters.<sup>11</sup> Similar reactions of simple aliphatic nitrites to yield  $\delta$ -hydroxynitroso compounds have recently been described by Kabasakalian and Townley.<sup>12</sup>

As Greene<sup>13</sup> and we<sup>14</sup> have shown, photolysis or thermal decomposition of *t*-hypochlorites provides a very convenient means of generating and studying the reactions of *t*-alkoxy radicals. When the alkoxy radical possesses a long enough side chain to permit a 1,5-

(1) Taken from the Ph.D. Thesis of Albert Padwa, Columbia University, 1962. Support of this work by the National Science Foundation is gratefully acknowledged.

(2) University Fellow, 1961-1962.

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(13) F. D. Greene, *ibid.*, **81**, 2688 (1959).

(14) C. Walling and B. B. Jacknow, *ibid.*, **82**, 6108 (1960), and subsequent papers.