

lutidinium bromide or tosylate. The solubility of HBr in TFE is low, and in the unbuffered solvolysis of **3-Br** the cell had to be carefully sealed in order to avoid evaporation of the HBr. The spectrophotometric measurements were conducted with a Gilford 2400-S spectrophotometer at 228 nm, where the difference in the absorptions of the starting materials and products is the largest. The rate constants for the first-order reaction were calculated by the KINDAT program.<sup>77</sup>

**Reaction of 3-OTs with Br<sup>-</sup>.** A mixture of 0.021 *M* **3-OTs**, 0.021 *M* 2,6-lutidine, and 0.025 *M* Et<sub>3</sub>NBr in TFE was kept at 35°. Samples were quenched with aqueous AcOH, and the Br<sup>-</sup> was titrated potentiometrically. After 40 min a sample was cooled, quenched with water, extracted (CH<sub>2</sub>Cl<sub>2</sub>), washed with water, AgNO<sub>3</sub> solution, dilute AcOH, and NaHCO<sub>3</sub> solution, and dried. The solvent was evaporated, and nmr analysis (CCl<sub>4</sub>) by integration of the Me

and MeO signals gave **3-Br** (83 ± 2%), **3-OTs** (5 ± 2%), and **4** (12 ± 2%).

**Reaction of 1-OTs with OTs<sup>-</sup>.** A mixture of 0.059 *M* **1-OTs**, 0.096 *M* triethylamine, and 0.36 *M* Et<sub>3</sub>NOTs in TFE was kept at 35°. Samples were poured into a 1:1 mixture of CCl<sub>4</sub> and water. The organic layer was separated, washed (water, AcOH, dilute NaHCO<sub>3</sub> solution), dried (MgSO<sub>4</sub>), and evaporated. The remainder was analyzed by nmr in CCl<sub>4</sub>. The progress of the reaction was evaluated from the ratios of the following signals: (a) Me (δ 1.43) [1-OR]/Me (δ 1.60) [1-OTs]; (b) MeO (δ 3.79) [1-OR]/MeO (δ 3.60) [1-OTs]; (c) Me (δ 2.33) [1-OTs]/overall Me or overall MeO. These ratios differed by ≤ 2% and their average was used.

**Acknowledgments.** We thank the Volkswagen Foundation for support of this work, Professors P. v. R. Schleyer and E. M. Kosower for helpful discussions, and Mr. F. Schadt for fruitful criticism.

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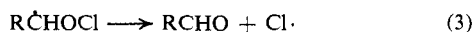
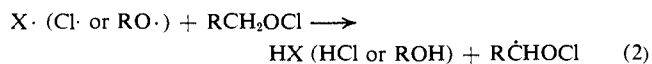
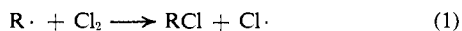
## Reactions of Primary and Secondary Alkoxy Radicals Derived from Hypochlorites<sup>1</sup>

Cheves Walling\* and Roger T. Clark

Contribution from the Department of Chemistry, University of Utah, Salt Lake City, Utah 84112. Received December 28, 1973

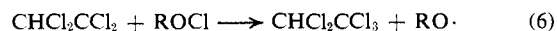
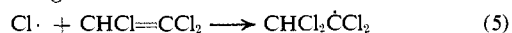
**Abstract:** By the use of suitable chlorine atom traps, *e.g.*, trichloroethylene, primary and secondary alkyl hypochlorites may be used as effective radical chlorinating agents, and the chemistry of the corresponding alkoxy radicals examined. The amount of β scission, in competition with reaction with cyclohexane, decreases roughly 100-fold in the order tertiary alkoxy > secondary alkoxy > primary alkoxy (for loss of the same radical, R<sub>1</sub>) with a corresponding increase in activation energy, the order correlating with decreasing π-bond energy of the carbonyl compound formed. Within the same class of alkoxy radical, ease of β scission parallels stability of the radical R<sub>1</sub> formed. β scission also shows a marked polar effect (for substituted benzyl radical loss ρ<sup>+</sup> = -1.04). In reaction with substrates (both selectivity between primary, secondary, and tertiary hydrogen and in the competition between olefin substitution and addition) primary, secondary, and tertiary alkoxy radicals show only small differences, but polar additions of primary and secondary hypochlorites are difficult to suppress.

The chemistry of the *tert*-butoxy (and other tertiary alkoxy) radicals has been investigated extensively, for the most part *via* either the decomposition of suitable peroxides or study of radical chain chlorinations using the corresponding hypochlorites.<sup>2</sup> Primary and secondary alkoxy radicals are less readily accessible, and chain chlorinations with primary and secondary hypochlorites are greatly complicated by induced decomposition suggested<sup>3</sup> as occurring *via* chlorine atom chains, *e.g.*



Chlorine atom chains are also occasional complications in the decomposition of tertiary hypochlorites, but here they can be successfully repressed by the use of negatively substituted olefins (which react readily with

halogen atoms, but not with alkoxy radicals) as chlorine atom traps,<sup>4,5</sup> *e.g.*



Some time ago it occurred to us that the same technique could be applied to minimize induced decomposition and eliminate chlorine atom chains in the reactions of primary and secondary hypochlorites, and we have shown that in the presence of di- and trichloroethylene, those with long side chains can be converted to δ-chloro alcohols *via* intramolecular chlorination in high, and sometimes almost quantitative, yield.<sup>6</sup>

This paper describes application of the same technique to short-chain hypochlorites, aimed at investigating the ease of β scission and selectivity in reaction of a number of primary and secondary alkoxy radicals derived from the corresponding hypochlorites.

### Results and Discussion

**β Scission of Alkoxy Radicals.** In the radical chain decomposition of alkyl hypochlorites in the presence

(1) Taken from the Ph.D. Thesis of R. T. Clark, University of Utah, 1973. Support of this work by grants from the National Science Foundation (GP 24300 and GP 36620) is gratefully acknowledged.

(2) C. Walling, *Pure Appl. Chem.*, **15**, 69 (1967).

(3) C. Walling, "Free Radicals in Solution," Wiley, New York, N. Y., 1957, p 388.

(4) C. Walling and J. A. McGuinness, *J. Amer. Chem. Soc.*, **91**, 2053 (1969).

(5) A. A. Zavitsas and J. D. Blank, *J. Amer. Chem. Soc.*, **94**, 4603 (1972).

(6) C. Walling and D. Bristol, *J. Org. Chem.*, **37**, 3514 (1972).

Table I.  $\beta$  Scission of Primary, Secondary, and Tertiary Alkoxy Radicals  $R_1R_2R_3CO\cdot$ 

$R_1$	$R_2$	$R_3$	Temp, °C	$k_d/k_a$	$E_d - E_a$ , kcal/mol	Log $A_d/A_a$
Et	Me	Me	30	1.37	4.11	3.09
			50	2.03	(3.96) <sup>a</sup>	
			70	3.04	(3.3) <sup>b</sup>	
Et	Me	H	30	0.250	4.53	2.66
			50	0.384		
			70	0.603		
Et	H	H	30	0.00266	11.11	5.45
			50	0.00849		
			70	0.0227		
<i>i</i> -Pr	Me	Me	30	72.7	1.84	3.18
			50	87.8	(1.29) <sup>a</sup>	
			70		(1.7) <sup>b</sup>	
<i>i</i> -Pr	Me	H	30	27.0	1.98	2.88
			50	35.0		
			70	41.9		
<i>i</i> -Pr	H	H	30	1.027	3.97	2.85
			50	1.465		
			70	2.103		
<i>t</i> -Bu	H	H	30	12.0	~0	
			50	19.4		
			70	17.7		
Benzyl	H	H	30	4.86	0.261	0.88
			50	5.10		
			70	5.11		
$(CH_2)_4^c$	$(CH_2)_4$	H	30	33.4	2.7	3.47
			50	44.3		
			70	56.3		

<sup>a</sup> Reference 9. <sup>b</sup> Reference 8. <sup>c</sup>  $R_1R_2R_3CO\cdot$  = cyclopentylloxy.

of a hydrocarbon substrate, substrate chlorination competes with  $\beta$  scission of the chain carrying alkoxy radical *via* the competing sequences



and



These competitions have been studied with a variety of tertiary hypochlorites<sup>4,7-9</sup> and the rate constant ratio  $k_a/k_d$  determined most accurately by measuring alcohol (or RCl) to carbonyl product (or  $R_1Cl$ ) ratios at a number of substrate concentrations. Here, if chains are long and chlorine atom chains eliminated,<sup>10</sup> the slope of plots of these ratios against  $[RH]$  yields  $k_a/k_d$ .<sup>9</sup>

We have now applied this technique to several primary and secondary hypochlorites, using cyclohexane as substrate as in a previous study<sup>4</sup> in the presence of trichloroethylene as a chlorine atom trap. A typical set of results, for 2-butyl hypochlorite at 30°, is shown in Figure 1 and all results are summarized in Table I. In general, analyses were made for cyclohexyl chloride/ $R_1Cl$  ratios, but in a few cases analysis for other ratios gave good checks.

For two tertiary cases,  $R_1$  = ethyl and isopropyl, activation parameters are compared with literature values, obtained in  $CCl_4$  solvent. Results are in fair

(7) F. D. Greene, *J. Amer. Chem. Soc.*, **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) C. Walling and A. Padwa, *J. Amer. Chem. Soc.*, **85**, 1593 (1963).

(9) C. Walling and P. J. Wagner, *J. Amer. Chem. Soc.*, **86**, 3368 (1964).

(10) The incursion of  $Cl\cdot$  chains, since they give rise to additional alcohol and RCl, leads to anomalously low  $k_a/k_d$  ratios.

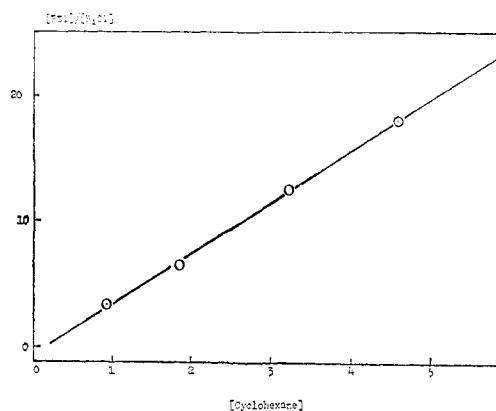


Figure 1. Reaction of 2-butyl hypochlorite with cyclohexane at 30°.

agreement, but it should be recalled that  $k_d/k_a$  ratios may show rather large solvent effects, and need to be compared in the same medium. In the case of *tert*-butoxy radicals Walling and Wagner<sup>9</sup> concluded that chloroethylenes stabilize the transition state for  $\beta$  scission, but they also noted that the magnitude and even direction of solvent effects changed rather unpredictably with the nature of  $R_1$ .

In considering the significance of the data of Table I, we assume that  $k_a$ 's are essentially constant and relative ratios are thus dependent on  $k_d$ 's.<sup>11</sup> For this reason ratios are given as  $k_d/k_a$ , the reciprocals of slopes from plots such as Figure 1. For primary, and secondary alkoxy radicals (as shown previously for tertiary cases),  $k_d$  increases with the stability of  $R_1\cdot$ , the radical produced on  $\beta$  scission. In fact, for secondary and tertiary alkoxy radicals, when  $R_1$  = *tert*-butyl or benzyl, only

(11) This assumption is based on the fact that  $D(RO-H)$  is essentially independent of  $R$ , so H abstractions by all alkoxy radicals are isoenergetic, and has been made in all previous discussions.

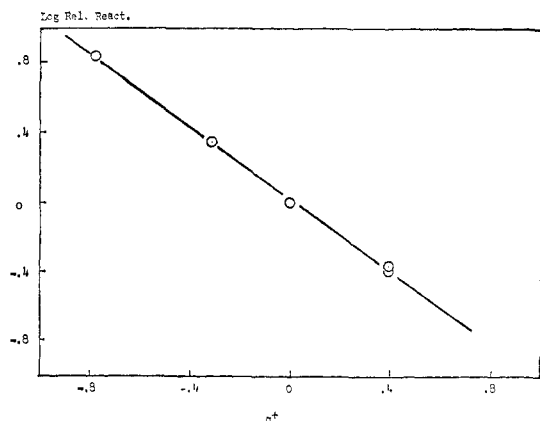


Figure 2. Hammett  $\rho^+\sigma^+$  relation for  $\beta$  scission of substituted benzyl radicals.

cleavage products are detected and no ratios can be determined.<sup>12</sup> For primary alkoxy radicals the sequence is Et < *i*-Pr < benzyl < *tert*-butyl. The inversion of benzyl and *tert*-butyl from expectation is discussed further below, but we may note that a similar inversion has been reported in the oxidative cleavage of tertiary alcohols by ceric ion.<sup>13</sup> More interesting, since quantitative data have not previously been available, are the relative rates of cleavage of the *same* R<sub>1</sub> from different alkoxy radicals. Here the order is clearly primary < secondary < tertiary with relative rates paralleling activation energy differences and tertiary alkoxy radicals undergoing cleavage roughly 100 times as rapidly as primary in our temperature range. This again appears to be an example of rate paralleling reaction energetics, and we propose that the major variable providing the difference in driving force here is the strength of the C–O  $\pi$  bond in the carbonyl group being formed. Thus, as illustration of these differences, heats of hydrogenation of formaldehyde, acetaldehyde, and acetone are –20.4, –16.4, and –13.2 kcal/mol, respectively, calculated from standard heats of formation.

Relief of steric strain may also contribute somewhat to both series, but, if it were dominant we would anticipate the *greatest* differences between isopropyl and *tert*-butyl when cleavage gives the same carbonyl product and between secondary and tertiary alkoxy radicals when the same radical is eliminated. For primary alkoxy radicals at 50°, relative rates at 50° are actually 1:173:2285 for ethyl, isopropyl and *tert*-butyl, and the relative rate of elimination from primary, secondary, and tertiary alkoxy radicals is 1:45:239 for ethyl and 1:24:60 for isopropyl. However, relief of steric strain is evidently important in the cyclopentylloxy radical, which undergoes  $\beta$  scission (with ring opening) over 100 times as rapidly as does the 2-butoxy radical. A similar difference was previously noted for the 1-methylcyclopentylloxy radical compared with the *tert*-pentylloxy radical.<sup>8</sup>

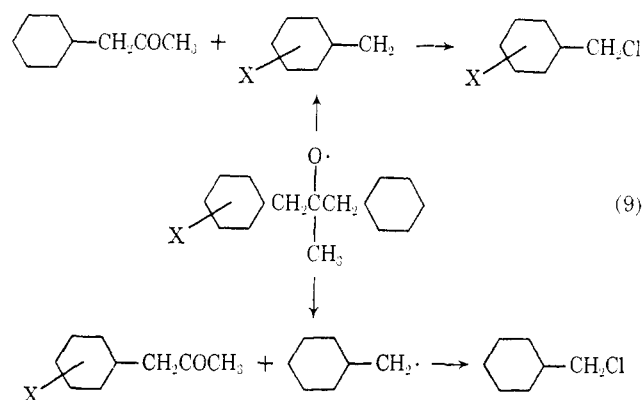
From Table I,  $k_d/k_a$  ratios in general parallel activation energy differences,  $E_d - E_a$ . Although the precision of our data is considerably better, allowing for undetected systematic errors we estimate that our activation energy differences are reliable to  $\pm 0.5$  kcal/mol with the excep-

(12) Previously reported ratios for R<sub>1</sub> = benzyl<sup>8,9</sup> have subsequently been shown to arise from incursion of Cl· chains.<sup>1</sup>

(13) W. S. Trahanovsky and D. B. Macaulay, *J. Org. Chem.*, **38**, 1497 (1973).

tion of the anomalously large value for the 1-propoxy radical where small  $k_d/k_a$  values made accurate analysis difficult. On the other hand, ratios of  $A$  factors show considerable scatter (in part due to experimental uncertainty) and evidence no discernible pattern.

**Polar Effects in  $\beta$  Scission.** Although overall energetics appear dominant in determining the ease of  $\beta$ -scission reactions of alkoxy radicals, Walling and Padwa<sup>8</sup> have proposed that the 10–20-fold lower rate of cleavage of CH<sub>2</sub>Cl compared with ethyl may indicate a considerable polar effect in the process, and a similar explanation could account for the more rapid cleavage of *tert*-butyl compared with benzyl noted here.<sup>14</sup> We have looked into the matter further by examining the ease of cleavage of substituted benzyl radicals with electron-supplying and -withdrawing groups from suitable alkoxy radicals by two techniques. In the first, which was generally successful, unsymmetric dibenzylmethylcarbinyl hypochlorites were decomposed, and the relative yields of benzyl and substituted benzyl chlorides were determined. In the second (successful only with nega-



tively, substituted derivatives, since electron-supplying groups led to large amounts of byproducts) substituted  $\beta$ -phenylethyl hypochlorites were decomposed in the presence of cyclohexane, and relative yields of  $\beta$ -scission and hydrogen-abstraction products were determined as in Table I. Results are listed in Table II, and give a

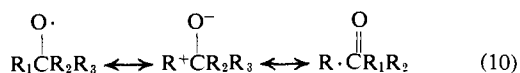
Table II.  $\beta$  Scission of Substituted Benzyl Radicals<sup>a</sup>

Substituent	Rel rate	Substituent	Rel rate
<i>p</i> -OCH <sub>3</sub>	6.95	<i>m</i> -Cl	0.40
<i>p</i> -CH <sub>3</sub>	2.21	<i>m</i> -Cl	0.43 <sup>b</sup>
None	1.00		

<sup>a</sup> From decomposition of dibenzylmethylcarbinyl hypochlorites at 30° in CCl<sub>4</sub> except as indicated. <sup>b</sup> Decomposition of  $\beta$ -(*m*-chlorophenyl)ethyl hypochlorite at 30° in the presence of cyclohexane and comparison with  $\beta$ -phenylethyl hypochlorite.

good correlation with  $\sigma^+$  constants,  $\rho^+ = -1.04$ , and correlation coefficient 0.9993, Figure 2 (for  $\sigma$  constants  $\rho = -1.69$ , but the correlation coefficient is only 0.973). Although the data are limited, they are consistent with contributions of polar structures to the transition state of the cleavage reaction (eq 10) and the magnitude of the effect is comparable to that observed in the thermal decomposition of *tert*-butyl phenylperacetates ( $\rho^+ =$

(14) Alternatively, the small value of  $A_d/A_a$  might imply special steric requirements in the transition state for benzyl cleavage in order to provide overlap between the  $\pi$  system and the developing radical.



−1.04 to −1.20),<sup>15</sup> for which very similar transition-state structures may be written. Unfortunately this conclusion is not unequivocal since, in the experiments involving cleavage of unsymmetric dibenzylmethylcarbinyl hypochlorites, the effect of substituents on the relative stabilities of the two possible product ketones should shift cleavage in the same direction. However, in the comparison of phenyl with *p*-chlorophenyl, where cleavage was also compared with hydrogen abstraction from cyclohexane, the two measurements gave essentially the same result.

**Addition vs. Hydrogen Abstraction.** A striking feature of the reaction of *tert*-butoxy radicals is their preference for hydrogen abstraction over double bond addition,<sup>16</sup> a property which makes *tert*-butyl hypochlorite a highly effective allylic halogenating reagent. No convincing explanation of this property has been advanced, but it was of interest to see whether primary and secondary alkoxy radicals show similar behavior. Isobutylene (reported to give 17.1% addition with *tert*-butyl hypochlorite)<sup>16</sup> was chosen as a convenient substrate, but experiments using *n*- and isopropyl hypochlorites gave complex and irreproducible results. Not only did relative yields of methallyl chloride and addition products vary, but the latter consisted of both 1-chloro-2-methyl-2-propyl ethers (the “Markovnikov” product) and 2-chloro-2-methyl-1-propyl ethers (the “anti-Markovnikov” product), indicating that both polar and radical processes were taking place. Since no reaction occurred between isopropyl hypochlorite and isobutylene in the dark after 24 hr at −10°, it seemed likely that the polar reaction was catalyzed by traces of HCl produced in the photoinitiated process, and conditions were sought to eliminate this difficulty. Best results were finally obtained by preparing all reagents in the dark, and initiating reaction with azobisisobutyronitrile in the presence of solid K<sub>2</sub>CO<sub>3</sub>. Our findings are summarized in Table III in which typical

Table III. Olefin Chlorinations by ROCl

R	Olefin	Condi- tions <sup>a</sup>	% addition	Radical/ polar addition	<i>k</i> <sub>ad</sub> / <i>k</i> <sub>s</sub> <sup>b</sup>
<i>t</i> -Bu	Isobutylene	A	16.8	4.39	0.222
		B	18.2	300	
<i>i</i> -Pr	Isobutylene	A	20.9	2.71	0.402
		B	32.1	12.4	
<i>n</i> -Pr	Isobutylene	A	25.9	0.206	0.521
		B	34.2	8.5	
<i>t</i> -Bu	Cyclohexene	A	2.93		0.039
		B	3.76		
<i>i</i> -Pr	Cyclohexene	A	9.85		0.154
		B	13.31		
<i>n</i> -Pr	Cyclohexene	A	12.42		0.119
		B	10.67		

<sup>a</sup> A = photoinitiated, room temperature; B = AIBN initiated + K<sub>2</sub>CO<sub>3</sub>, 60°. <sup>b</sup> Ratio of rate constants for radical addition and substitution.

photoinitiated experiments are compared with those obtained under optimum conditions. The relative con-

(15) P. D. Bartlett and C. Ruchardt, *J. Amer. Chem. Soc.*, **82**, 1756 (1960).

(16) C. Walling and W. Thaler, *J. Amer. Chem. Soc.*, **83**, 3877 (1961).

Table IV. Competitive Chlorination of Cyclohexene and Cyclohexane by *tert*-Butyl Hypochlorite (40°)

Solvent	% conversion	Analysis <sup>a</sup>	Rel reactivity (C <sub>6</sub> H <sub>10</sub> /C <sub>6</sub> H <sub>12</sub> )
CCl <sub>4</sub>	15	SM	5.56
CCl <sub>4</sub>	15	P	5.28
CCl <sub>4</sub>	25	SM	10.3
CCl <sub>4</sub>	45	SM	11.6
Freon 112	20	SM	8.46 <sup>b</sup>
C <sub>2</sub> HCl <sub>3</sub>	19	P	4.52
C <sub>2</sub> HCl <sub>3</sub>	38	SM	5.97

<sup>a</sup> SM = analysis by disappearance of starting material, P = appearance of products. <sup>b</sup> From ref 16.

Table V. Selectivity in Chlorination by ROCl (40°)

R	Substrate <sup>a</sup>	<i>k</i> <sub>t</sub> / <i>k</i> <sub>p</sub>	<i>k</i> <sub>p</sub> / <i>k</i> <sub>s</sub>
<i>n</i> -Pr	DMB-CH	128.	2.4
	TMB	28.4	
<i>i</i> -Pr	DMB-CH	81.7	2.16
	TMB	25.0	
<i>t</i> -Bu	DMB-CH	56.7 (44.5) <sup>b</sup>	(2.80) <sup>b</sup>
	TMB	25.4	

<sup>a</sup> DMB = 2,3-dimethylbutane; CH = cyclohexane; TMB = 2,2,3-trimethylbutane. <sup>b</sup> C. Walling and B. B. Jacknow, *J. Amer. Chem. Soc.*, **82**, 6108 (1960).

tributions of ionic and polar paths were determined from the composition of the chloro ethers produced, and the values of *k*<sub>ad</sub>/*k*<sub>s</sub> listed were corrected accordingly. With cyclohexene, the two paths give the same chloro ether, and we can only assume that the K<sub>2</sub>CO<sub>3</sub> technique effectively eliminates the polar path. From Table III it is evident that the relative contribution of addition is larger for primary and secondary alkoxy radicals (suggesting some steric hindrance to addition with *tert*-alkoxy radicals) but that attack on allylic hydrogen still remains the faster process.

A second puzzling feature of *tert*-butyl hypochlorite chlorinations is the reported abnormally high overall reactivity of cyclohexene compared with other olefins,<sup>16</sup> and we have also looked into this question by reexamining the competitive chlorination of cyclohexene and cyclohexane. Results are summarized in Table IV, where we find that the relative reactivity of cyclohexene apparently increases with conversion (and is accompanied by increasing yields of addition products). This increase disappears in the presence of trichloroethylene, and it seems likely that the previous measurement included some contribution from polar addition. Our average value for relative reactivity (cyclohexene/cyclohexane) at low conversion or in the presence of a Cl· trap is 5.12, giving a relative reactivity per H of 14.8 vs. cyclohexane, compared with 24.4 reported previously. For reference, the relative reactivity of secondary hydrogens in *cis*-2-pentene has been reported as 6.09, so the anomaly is at least considerably reduced.

**Selectivity in Hydrogen Abstraction.** Finally, we have examined briefly the selectivity of primary and secondary alkoxy radicals toward primary, secondary, and tertiary hydrogen, using 2,2,3-trimethylbutane and 2,2-dimethylbutane-cyclohexane mixtures as substrates and determining the composition of the resulting chlorides (Table V). In general results differ little from those obtained with *tert*-butyl hypochlorite, although

the increased tertiary/primary ratios observed with 2,3-dimethylbutane suggest that steric hindrance may reduce the reactivity of tertiary hydrogens toward highly substituted alkoxy radicals.

In summary, there appears to be no major differences in reactivity of alkoxy radicals of differing structure, either in their selectivity toward different C-H bonds, or in the competition between addition and hydrogen abstraction, strongly suggesting that, in the same system, their reactions with a substrate occur at comparable rates. On the other hand, there are enormous differences in the rates at which they undergo  $\beta$  scission; loss of a benzylic or tertiary radical from a tertiary alkoxy radical proceeds over  $10^5$  times as rapidly as loss of a primary radical from a primary alkoxy radical. These differences must be highly significant in a number of technical reactions in which alkoxy radicals play an important role, e.g., hydrocarbon autoxidation and the oxidative degradation of polymers, and need to be taken into account in interpreting the large changes in rate and reaction course which occur with change of structure in such systems.

## Experimental Section

**Materials** were commercial reagents when available or were prepared by standard procedures (except as noted), purified by conventional means as necessary and purity checked by glc analysis. **Hypochlorites** were prepared from the corresponding alcohols, NaOCl solution, and acetic acid, essentially as in previous work.<sup>4</sup> Except for *tert*-butyl hypochlorite, they were not isolated but prepared in the appropriate solvent (usually  $\text{CCl}_4$ ), washed, and dried, and concentrations were determined by iodometric titration.  $\beta$ -Chloro ethers needed for reference ("Markovnikov" products) were prepared by a  $\text{BF}_3$  catalyzed reaction of *tert*-butyl hypochlorite and a large excess of the appropriate alcohol with the appropriate olefin as described elsewhere.<sup>17</sup> "Anti-Markovnikov" ethers were isolated from reaction mixtures by preparative glc.

**Reactions** were carried out in sealed, degassed tubes as in previous papers, and analyzed by glc. In  $\beta$ -scission experiments, all reactions were 4 M or higher in trichloroethylene. Experiments with isobutyl and 3-methyl-2-butyl hypochlorites were carried out at 0, 30, and 60°, Arrhenius parameters were calculated from these data, and the results in Table I were obtained by interpolation and extrapolation. Data were analyzed as in previous papers, and all slopes of linear plots reported were obtained by least-squares fitting of the data.

(17) C. Walling and R. T. Clark, *J. Org. Chem.*, **39**, 1962 (1974).

## Reaction of Alkenes with Hydrogen Bromide in Acetic Acid. Polar Addition *via* the Ad3 Mechanism<sup>1</sup>

Robert C. Fahey,\* C. Allen McPherson, and Robert A. Smith

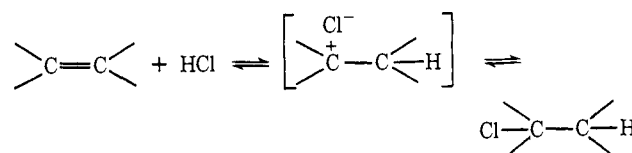
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**Abstract:** The rates and products for the polar reaction of cyclohexene and 1-hexene with HBr in acetic acid have been measured at 25°. The results are consistent with an Ad3 mechanism involving bromide ion catalysis for HBr addition and with an Ad3 mechanism involving HBr catalysis for HOAc addition. Studies with cyclohexene-1,3,3-*d*<sub>3</sub> show that HOAc and HBr add with a strong preference for anti addition between 15 and 60°. Factors influencing ion pairing in the Ad3 transition state and the relationships between Ad3 and E2 reactions are discussed.

Prompted by a report by Smirnov-Zamkov and Piskovitina<sup>2</sup> that DBr addition to cyclohexene in DOAc yields a mixture of syn and anti adduct in which the syn:anti ratio increases from ~0.3 to ~3 between 10 and 60°, we undertook, some years ago, a study of HBr addition to cyclohexene-1,3,3-*d*<sub>3</sub> in acetic acid in order to elaborate the origin of this interesting temperature effect. Our own results<sup>1</sup> differed from the earlier findings in that both HOAc and HBr adducts were observed, and both adducts resulted from predominant or exclusive anti addition in the temperature range 15–60°. Initial efforts to elaborate the kinetics of the reaction of cyclohexene with HBr in HOAc suggested a rather complex rate law and, fearing complications from competing homolytic reactions, we turned to a study of HCl addition.

In recent years we have reported a number of studies of the reaction of HCl with olefins and acetylenes which clarify the mechanism for polar addition of HCl to unsaturated hydrocarbons. For simple alkenes and

arenes two mechanisms are important. One involves reaction *via* a carbonium ion intermediate (Ade2 mechanism), formed as an ion pair in ion-pairing solvents, and is formally the reverse of the E1 elimination process.<sup>3</sup>



The second mechanism occurs *via* a transition state involving both C-H and C-Cl bond formation (Ade3 or Ad3 mechanism)<sup>4</sup> and is formally the reverse of the E2 elimination process.<sup>5,6</sup>

(3) R. C. Fahey and C. A. McPherson, *J. Amer. Chem. Soc.*, **91**, 3865 (1969).

(4) We have previously used the designation Ade3 but now feel that the more general designation Ad3 is to be preferred until the detailed electronic structure of the transition state is elaborated.

(5) R. C. Fahey, M. W. Monahan, and C. A. McPherson, *J. Amer. Chem. Soc.*, **92**, 2810 (1970); R. C. Fahey and M. W. Monahan, *ibid.*, **92**, 2816 (1970).

(6) R. C. Fahey and C. A. McPherson, *J. Amer. Chem. Soc.*, **93**, 2445 (1971).

(1) Reported in part in a preliminary communication: R. C. Fahey and R. A. Smith, *J. Amer. Chem. Soc.*, **86**, 5035 (1964).

(2) J. V. Smirnov-Zamkov and G. A. Piskovitina, *Ukr. Khim. Zh.*, **28**, 531 (1962).