

# Ground- and Excited-State Carboxylate Radical Chain Carriers. Radical Chain Substitution Reactions with Acyl Hypohalites

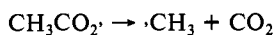
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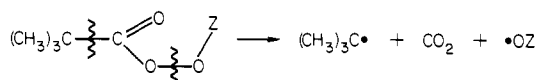
**Abstract:** Earlier work with aliphatic carboxylate radicals held no prospect that they could be used as hydrogen abstractors in substitution reactions. Contrary to this expectation, acetoxy, propionoxy, isobutyroxy, and pivaloxy are effective in this role. At low temperatures radical chain brominations of alkanes and haloalkanes occur in satisfactory yields when the acyl hypobromites,  $\text{RCO}_2\text{Br}$ , are used; the selectivities are independent of the structure of R. Two distinctive hydrogen-abstracting  $\text{RCO}_2\cdot$  are involved in these chain reactions, either the  $\pi$  or  $\sigma_a$  electronic states; which electronic state is the chain carrier is determined in the step  $\text{RCO}_2\text{Br} + \text{X}\cdot \rightarrow \text{RCO}_2\cdot + \text{XBr}$ . These  $\text{C}_\pi$  and  $\text{C}_\sigma$  radicals resemble *tert*-butoxy in their hydrogen-abstraction selectivities. The concordance of these results with a state-of-the-art calculation is discussed.

There is a wide acceptance of the paradigms that (a) excited states play no role in thermal processes and (b) decarboxylation of aliphatic carboxylate radicals,  $\text{RCO}_2\cdot$ , is so rapid that only cage reactions can be observed.<sup>2-4</sup> For acetoxy, a decarboxylation rate constant at 60 °C of  $1.6 \times 10^9 \text{ s}^{-1}$  has been deduced.<sup>5</sup>



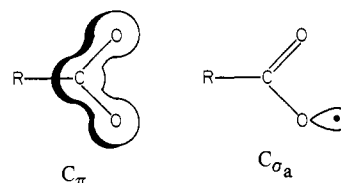
$$\log k = 13.55 - (6600/2.3RT)$$

For pivaloxy ( $(\text{CH}_3)_3\text{CCO}_2$ ), a larger rate of decarboxylation has been suggested.<sup>6</sup> It is proposed that thermolyses of peroxy-pivaloyl compounds proceed with concerted breaking of two bonds, thus bypassing the pivaloxy radical.<sup>7</sup>



By contrast, if carboxylate radicals are generated in thermo-neutral or exothermic steps, rather than the highly endothermic peroxide homolyses ( $E_{\text{act}} = 30\text{--}40 \text{ kcal/mol}$ ),<sup>8</sup> the bimolecular chemistry of these carboxylate radicals can be studied in competition with the decarboxylation reactions because it becomes possible to examine their reactions at lower temperatures.

The conclusions from these studies depart from conventional wisdom: (1) Aliphatic carboxylate radicals react by hydrogen abstraction in close competition with decarboxylation; (2) the selectivities in hydrogen abstractions are independent of the structure of R; (3) the selectivities are characteristic of early transition state hydrogen abstractions, similar to the *tert*-butoxy radical; (4) two distinctive hydrogen abstracting carboxylate radicals can be generated in thermal chain reactions, labeled  $\text{C}_\pi$  and  $\text{C}_\sigma$ , distinguished from a third state,  $\text{C}_{\sigma_a}$ , which we have not been able to generate; (5) at low temperatures pivaloxy decar-



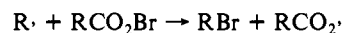
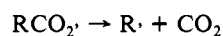
boxylates less rapidly than acetoxy; (6) the activation energy for loss of carbon dioxide is larger for pivaloxy than for acetoxy. Conclusions 1–5 are the subjects of this paper; treatment of the last will be published in the near future. For the present paper, 37 tables of data have been relegated to Supplementary Material.

The possibility that H abstraction by acetoxy rather than Hunsdiecker reaction would be observed at low temperatures is reasonable if these H abstractions occur with lower  $E_{\text{act}}$ . At  $-80 \text{ }^\circ\text{C}$  the rate of decarboxylation of acetoxy is calculated as  $1.4 \times 10^6 \text{ s}^{-1}$ .

The possibility that carboxylate radicals can exist in different electronic states was first suggested in a pioneering paper by Koenig and Wielessek.<sup>9</sup> From INDO calculations, they concluded that there are three low-lying carboxylate radical states ( $\text{C}_{2v}$  symmetry). These states have the unpaired electron in different orbitals and should each display their own unique chemistry. Recent ab initio calculations by Peyerimhoff et al.<sup>10</sup> and Davidson et al.<sup>11</sup> have placed the energy spacing of these three levels on the order of 14 and 18 kcal/mol, respectively. Dewar et al.<sup>46</sup> indicate an energy separation less than 5 kcal/mol for the lowest two states.

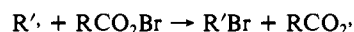
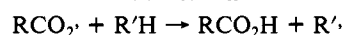
The Hunsdiecker reaction involves the conversion of acyl hypohalites  $\text{RCO}_2\text{X}$ , to  $\text{RX}$  and  $\text{CO}_2$ .<sup>12</sup> There is no report that

Hunsdiecker



substitution reactions on solvent or other substrates occur as competing reactions. At room temperature we find these sub-

stitution



(1) From: May, D. D. Ph.D. Thesis, The Pennsylvania State University, 1982.

(2) Herk, L.; Feld, M.; Szwarc, M. *J. Am. Chem. Soc.* **1961**, *83*, 2998–3005.

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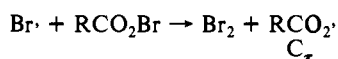
(11) Feller, D.; Huyser, E. S.; Borden, W. T.; Davidson, E. R. *J. Am. Chem. Soc.* **1983**, *105*, 1459–1466.

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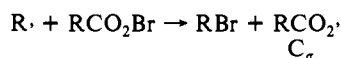
stitution reactions are minor pathways, but at low temperatures (< -60 °C) the substitution reactions can be a major pathway in these chain reactions (see ref 47).

Examination of the substitution reactions revealed two distinctly different substitution selectivities, which forced the assignment of two carboxylate radical states, labeled  $C_{\sigma_a}$  and  $C_{\sigma_r}$ . The formation of one or the other of these states depends solely on the carboxylate radical generating step: In method I  $Br_2$  is present; in method II  $Br_2$  is scavenged. A third carboxylate radical state,  $C_{\sigma_d}$ , which only decarboxylates,<sup>10</sup> is not generated under our reaction conditions. The analogous use of *N*-bromosuccinimide, instead of acyl hypobromites, generated succinimidyl radicals  $S_{\sigma_r}$  in method I and  $S_{\sigma_a}$  in method II conditions.<sup>13</sup>

#### Method I



#### Method II



### Experimental Design

Carboxylate radicals can be generated in low-temperature chain reactions using acetyl ( $MeCO_2Br$ ), propionyl ( $EtCO_2Br$ ), isobutyryl ( $i\text{-}PrCO_2Br$ ), and pivaloyl ( $t\text{-}BuCO_2Br$ ) hypobromites as well as acetyl hypochlorite ( $MeCO_2Cl$ ). Solutions of these acetyl hypohalites and substrates, in  $CCl_3F$  solvent, photoinitiated at temperatures of -60 °C to -100 °C, react by radical chain substitutions in yields as high as 55%, in competition with the Hunsdiecker reaction. The identity of the chain carriers must be established for this discussion. The selectivities displayed by the acyl hypohalites in competitive hydrogen abstractions do not vary with changes in the alkyl group of the acyl hypohalites, thus excluding alkyl radicals as the hydrogen-abstracting species.<sup>14-16</sup>

There are a number of lines of evidence that exclude a bromine atom chain in substitution reactions, one of which is the identity of the selectivities observed with acetyl hypochlorite and acetyl hypobromite. Second, bromine atom selectivities for abstraction from primary, secondary, and tertiary alkanic hydrogens ( $k_p:k_s:k_t$ ) can be calculated from well-documented data.<sup>17</sup> At -78 °C  $k_p:k_s:k_t$  is (1) : 10<sup>4</sup> : 10<sup>7</sup>. In acyl hypobromite mediated substitution reactions at -78 °C (method I)  $k_p:k_s:k_t$  is (1):10<sup>1.3</sup>:10<sup>2</sup> and (method II)  $k_p:k_s:k_t$  is (1):10<sup>1.0</sup>:10<sup>1.7</sup>.

A bromine-carbonyl chain carrier for H abstraction (suggested by referees), which might result from addition of  $Br\cdot$  to acyl hypobromite,  $CH_3C(OX)(Br)O\cdot$ , is unlikely on purely energetic grounds. However, this unknown type of intermediate, impossible to exclude on positive evidence, nonetheless, appears to be an unlikely candidate. For one, the substitution yields from acyl hypobromite mediated substitution reactions improve with increasing steric bulk in the order  $Me \sim Et < i\text{-}Pr < t\text{-}Bu$ , the reverse of predictions based on steric ground. The formation of this hypothetical adduct resembles the well-understood formation of tetracoordinate intermediates from carbonyl compounds and nucleophiles. Second, to mimic the addition of  $Br\cdot$  to carbonyl groups, attempts were made to carry out photobrominations of methylene chloride/neopentane (MC/N) mixtures in the presence of acetic acid, acetyl bromide, and hexafluoroacetone (Table I) under the same reaction conditions employed in the reactions of

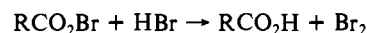
Table I. Reactions of Various Brominating Agents with Methylene Chloride/Neopentane at -78 °C<sup>a</sup>

brominating agent	amount <sup>c</sup>	yields <sup>b</sup>		
		$CHCl_2Br$	<i>neo</i> - $C_5H_{11}Br$	$S^d$
$CH_3CO_2Br/Br_2$	0.250/0.01	11.0	5.60	12
$Br_2/K_2CO_3$	0.050	7.6	0.38	120
$CH_3COBr/Br_2$	0.13/0.05	7.5	0.41	110
$CH_3CO_2H/Br_2$	0.10/0.01	1.5	0.15	60
$(CF_3)_2CO/Br_2$	0.15/0.05	7.4	0.39	114

<sup>a</sup> Degassed solutions consisting of 5 mL of Freon 11 and 10 mmol each of  $CH_2Cl_2$  and *neo*- $C_5H_{12}$  irradiated through Pyrex at -78 °C for 15 min with a medium-pressure mercury arc. <sup>b</sup> In  $\mu\text{mol}$ , determined by GC employing an internal standard. <sup>c</sup> Quantities of brominating reagents in mmol. <sup>d</sup> Per hydrogen; ( $\mu\text{mol}$  of  $CHCl_2Br/\mu\text{mol}$  of *neo*- $C_5H_{11}Br$ )  $\times$  6.

$MeCO_2Br$ . In each instance bromination with  $MeCO_2Br$  was faster and showed a different selectivity. Thus, it is unlikely that the reactions of acyl hypobromites proceed with a bromine atom-carbonyl complex as chain carrier.

It should be noted that although hydrogen abstraction by carboxylate radical produces carboxylic acid, monitoring the yield of carboxylic acid in the acyl hypohalite mediated substitution reactions, as a measure of carboxylate radical involvement, is ambiguous since the ionic reaction of hydrogen bromide (which would be produced in a bromine atom chain reaction) with acyl hypobromite would also produce carboxylic acid. In experiments



for which the yield of carboxylic acid was determined, it was found to be equal to the yield of substitution products.

The work described in this paper employed freshly prepared solutions of acyl hypohalites in  $CCl_3F$  solution, prepared in the reaction of silver carboxylates with bromine, that were filtered to remove silver bromide. Removal of  $CCl_3F$  solvent at -23 °C leaves white needlelike crystals of  $MeCO_2Br$  and  $EtCO_2Br$ , which were redissolved in  $CCl_3F$  solvent. The results from reactions run with these solutions of  $MeCO_2Br$  and  $EtCO_2Br$  were identical with those obtained from solutions that were only filtered. **Caution:** *Crystalline  $MeCO_2Br$  and  $EtCO_2Br$  are hazardous materials, exploding unpredictably.*

The recognition that two different states of carboxylate radical can be generated is manifested by the selectivities (vide infra) observed in hydrogen-abstraction reactions conducted under different reaction conditions: All details are identical except that method I has present  $Br_2$  at concentrations greater than 0.01 M and method II employs vinylidene chloride (VC) in quantities sufficient to remove all  $Br_2$  present in the acyl hypobromite solutions.<sup>18</sup> Other olefins are unsuitable as halogen scavengers due to the rapid ionic addition of acyl hypohalites.<sup>19</sup> Since quantitative yields of products are observed in method II reactions, loss of acyl hypohalites by reaction with VC is not important.

The focus of this paper is the determination of the relative rate constants for competitive hydrogen-abstraction reactions of carboxylate radicals generated under these two sets of conditions. The effect of varying the concentrations of bromine, olefin, and substrates as well as the effect of changing the alkyl group of the acyl hypobromite on these relative rate constants is reported. The effects of variation in temperature and of variations in the alkyl group of  $RCO_2\cdot$  on product yields and distributions have been described in a preliminary fashion.<sup>20</sup>

**Reactions of Acetyl Hypobromite.** In the absence of hydrogen donors,  $CCl_3F$  (Freon 11) solutions of acetyl hypobromite in the

(13) (a) Skell, P. S.; Day, J. C. *Acc. Chem. Res.* **1978**, *11*, 381-387. (b) Tlumak, R. L.; Skell, P. S. *J. Am. Chem. Soc.* **1982**, *104*, 7267-7274. (c) Tlumak, R. L.; Day, J. C.; Slanga, J. P.; Skell, P. S. *J. Am. Chem. Soc.* **1982**, *104*, 7257-7267.

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(15) McNesby, J. R.; Gordon, A. S. *J. Am. Chem. Soc.* **1956**, *78*, 3570-3573. References 14 and 15 for  $k_p:k_s:k_t$  methyl radical.

(16) Boddy, P. J.; Steacie, E. W. R. *Can. J. Chem.* **1960**, *38*, 1576-1589.  $k_p:k_s:k_t$  ethyl radical.

(17) Fettis, G. C.; J. H.; Trotman-Dickenson, A. F. *J. Chem. Soc.* **1960**, 4177-4185.

(18) Skell, P. S.; May, D. D. *J. Am. Chem. Soc.* **1981**, *103*, 967-968. In this preliminary report, we claimed no hydrogen abstraction under method II conditions. This error was the result of partial or total loss of acyl hypohalite to Hunsdiecker reaction products prior to addition of substrate. To overcome this problem, substrate is added at the same time as VC.

(19) Wilson, C. V. *Org. React. (N.Y.)* **1957**, 332-387.

(20) May, D. D.; Skell, P. S. *J. Am. Chem. Soc.* **1982**, *104*, 4500-4502.

Table II. Reactions of Acetyl Hypohalites with Methylene Chloride (1.46 M)/Neopentane (1.46 M) at  $-78^{\circ}\text{C}$ 

halogenating agent	yields <sup>a</sup>				<i>S</i> <sup>b</sup>	<i>A</i> <sup>c</sup>	no. of experiments
	MeX	CO <sub>2</sub> <sup>f</sup>	<i>neo</i> -C <sub>5</sub> H <sub>11</sub> X	CHCl <sub>2</sub> X			
CH <sub>3</sub> CO <sub>2</sub> Br/Br <sub>2</sub> <sup>d</sup>	92	91	2.15	4.23	12 ± 1	98	5
CH <sub>3</sub> CO <sub>2</sub> Br/VC <sup>e</sup>	92	90	3.04	3.63	7.2 ± 1	99	5
CH <sub>3</sub> CO <sub>2</sub> Cl/VC <sup>g</sup>	90	90	1.02	1.28	7.5 ± 1	92 <sup>g</sup>	3

<sup>a</sup> Yields (+5% of reported value) were determined by GC employing an internal standard and are expressed as percentages based on starting acyl hypohalite. <sup>b</sup> Selectivity calculated from the molar ratio (CHCl<sub>2</sub>X/*neo*-C<sub>5</sub>H<sub>11</sub>X) times (12 neopentane hydrogens/2 methylene chloride hydrogens). <sup>c</sup> 100 × (mmol of MeX + mmol of *neo*-C<sub>5</sub>H<sub>11</sub>X + mmol of CHCl<sub>2</sub>X)/mmol of AcOX. <sup>d</sup> 0.05 mmol of Br<sub>2</sub>; 0.250 mmol of MeCO<sub>2</sub>Br. <sup>e</sup> 0.62 mmol of VC; 0.250 mmol of MeCO<sub>2</sub>Br. <sup>f</sup> Carbon dioxide collected by trap-to-trap distillation ( $-130^{\circ}\text{C}$ ,  $-196^{\circ}\text{C}$ ) and measured volumetrically. <sup>g</sup> 6.0 M in VC; 0.500 mmol of MeCO<sub>2</sub>Cl. Trichloroethylene was produced in 7% yield, making the accounting 99%.

presence of bromine (MeCO<sub>2</sub>Br/Br<sub>2</sub>) and acetyl hypobromite in the presence of vinylidene chloride (MeCO<sub>2</sub>Br/VC) undergo photoinitiated Hunsdiecker reactions producing methyl bromide and carbon dioxide with yields in excess of 98% over temperature ranges spanning from  $-100$  to  $+10^{\circ}\text{C}$ . Photoinitiation of MeCO<sub>2</sub>Br/Br<sub>2</sub> or MeCO<sub>2</sub>Br/VC solutions containing methylene chloride and neopentane (MC/N) substrates at  $10^{\circ}\text{C}$  also gave 99% yield of methyl bromide and a 99% yield of carbon dioxide; bromodichloromethane and neopentyl bromide were not detected.<sup>47</sup>

In contrast to the quantitative formation of methyl bromide and carbon dioxide observed at  $10^{\circ}\text{C}$ , photoinitiated reactions at  $-78^{\circ}\text{C}$  of MeCO<sub>2</sub>Br/Br<sub>2</sub> solutions (0.05 and 0.01 M, respectively) containing 1.46 M each of neopentane and methylene chloride, in addition to Hunsdiecker products (92% methyl bromide and 91% carbon dioxide), produced the substitution products bromodichloromethane (4.23%) and neopentyl bromide (2.15%). The sum of the Hunsdiecker products and hydrogen-abstraction products accounts for over 98% of the starting MeCO<sub>2</sub>Br. On a per-hydrogen basis, methylene chloride is 12 times more reactive than neopentane toward hydrogen abstraction.

Photolysis at  $-78^{\circ}\text{C}$  of the same reaction mixture, except that VC replaces Br<sub>2</sub>, yields methyl bromide (92%) and carbon dioxide (90%), as well as bromodichloromethane (3.63%) and neopentyl bromide (3.04%). The sum of the decarboxylation and hydrogen-abstraction products accounts for 99% of the acetyl hypobromite. With MeCO<sub>2</sub>Br/VC, on a per-hydrogen basis, the hydrogens of methylene chloride are 7.2 times more reactive than the hydrogens of neopentane. These two key observations, distinctly different hydrogen-abstraction selectivities by the carboxylate radicals, are the basis for postulating two different carboxylate radical states. One type denoted  $\pi$  is generated in the presence of bromine (Method I) and the other denoted  $\sigma_a$  is produced under halogen scavenging (Method II). These results are summarized in Table II.

**Reactions of Acetyl Hypochlorite.** Halogenations using MeCO<sub>2</sub>Cl with a high concentration of vinylidene chloride (6.0 M) at  $-78^{\circ}\text{C}$  produce the decarboxylation products methyl chloride (90%) and carbon dioxide (90%) and the hydrogen-substitution products, chloroform (1.28%) neopentyl chloride (1.02%), and trichloroethylene (7%). On a per-hydrogen basis, the relative rate of hydrogen abstraction from methylene chloride is 7.2 times faster than from neopentane, the same as that obtained with MeCO<sub>2</sub>Br (see Table II). The similar selectivities exhibited by the MeCO<sub>2</sub>Cl/VC and MeCO<sub>2</sub>Br/VC experiments implicate a common hydrogen abstractor.

Halogenations with MeCO<sub>2</sub>Cl in the presence of small amounts of Cl<sub>2</sub> are dominated by chlorine atom chains, the neopentyl chloride to chloroform ratio varies from 10 to 100. Chlorination of MC/N with Cl<sub>2</sub> alone results in a ratio of neopentyl chloride to chloroform of 100:1.<sup>27,30</sup>

**Measurement of Quantum Yields.** The chain nature of these reactions was confirmed by measuring the quantum yield for the rate of disappearance of propionyl hypobromite (EtCO<sub>2</sub>Br) followed by iodometric titration (Table III). The selectivity toward hydrogen donors and the yields of substitution products were found to be similar for EtCO<sub>2</sub>Br and MeCO<sub>2</sub>Br. EtCO<sub>2</sub>Br was employed as a matter of convenience; it is more soluble at low temperatures.

The quantum yields for the disappearance of EtCO<sub>2</sub>Br at 313 ± 8 nm ( $\lambda_{\text{max}}$  319 nm,  $\epsilon$  200)<sup>21</sup> in systems that contain bromine,

Table III. Quantum Yields for the Disappearance of Propionyl Hypobromite at  $-78^{\circ}\text{C}$ <sup>a</sup>

reactants	substrates	minimum quantum yields <sup>b</sup>
EtCO <sub>2</sub> Br/Br <sub>2</sub> <sup>c</sup>	none	40 ± 10
EtCO <sub>2</sub> Br/Br <sub>2</sub> <sup>c</sup>	1-bromobutane <sup>e</sup>	40 ± 10
EtCO <sub>2</sub> Br/VC <sup>d</sup>	1-bromobutane <sup>e</sup>	40 ± 10

<sup>a</sup> Measured at 313 nm as disappearance of EtCO<sub>2</sub>Br vs. time.

<sup>b</sup> Assuming two chains started for each mole of photons absorbed.

<sup>c</sup> 0.250 mmol of EtCO<sub>2</sub>Br; 0.05 mmol of Br<sub>2</sub> in 5 mL of Freon 11.

<sup>d</sup> 0.250 mmol of EtCO<sub>2</sub>Br; 0.62 mmol of VC in 5 mL of Freon 11.

<sup>e</sup> 2.67 M; the yields of substitution products were ~10%, the remainder consisting of Hunsdiecker product and unreacted EtCO<sub>2</sub>Br.

with or without substrates, is 40. The quantum yields for the disappearance of EtCO<sub>2</sub>Br from reactions carried out under halogen-scavenging conditions are also 40. These are minimum values since they were calculated based on the assumption that the initiation step has 100% light efficiency, producing two free-radical chains per photon absorbed.

Thus, from methods I or II, the loss of EtCO<sub>2</sub>Br is a chain reaction. Since the major process in these experiments is the Hunsdiecker reaction, this is proof that the Hunsdiecker is a chain process. However, as will be shown later with kinetic criteria, the Hunsdiecker and substitution reactions are intimately coupled, thus indicating that the latter are also chain processes.

Irradiation of EtCO<sub>2</sub>Br/Br<sub>2</sub> solutions at 400 nm (interference filter with 20-nm bandwidth at half-peak intensity), a wavelength that only molecular bromine absorbs, causes initiation of these chain reactions by bromine atom. The individual yields of dibromobutanes (totaling 51%) are listed in Table IV. The ratio of the dibromobutanes produced is similar to that obtained from the reactions of EtCO<sub>2</sub>Br with 1-bromobutane with unfiltered broad-band medium-pressure mercury arc irradiation (Table IV). This observation indicates that a nonchain reaction of excited EtCO<sub>2</sub>Br, as suggested by a referee, such as direct formation of substitution products by a bimolecular reaction with substrate, is not occurring, further strengthening the attribution of the substitution reactions to chain processes.

**Effect of Olefin Concentration.** The effect of change in vinylidene chloride concentration on the yield of hydrogen-abstraction and decarboxylation products is described in Table V. Changes in the olefin concentration by a factor of 150, from 0.024 to 3.6 M, had no effect on the selectivity of propionoxy toward MC/N mixtures, its value remaining constant at 7.0. Thus, under method II conditions the olefin appears to serve only as a bromine scavenger; it is not directly involved in the substitution or decarboxylation reactions.

At high concentrations of vinylidene chloride 2-bromo-1,1-dichloroethylene is a readily observed substitution product.

**Effect of Bromine Concentration.** The data in Table VI demonstrate that changes in the ratio of the concentrations of Br<sub>2</sub> to EtCO<sub>2</sub>Br can affect the selectivity of propionoxy as a hydrogen abstractor. These data are shown graphically in Figure 1, a plot of the ratio of products bromodichloromethane to neopentyl

Table IV. Reaction of Propionyl Hypobromite/Bromine with 1-Bromobutane at  $-78^{\circ}\text{C}$ : Initiation by 400-nm Light<sup>a</sup>

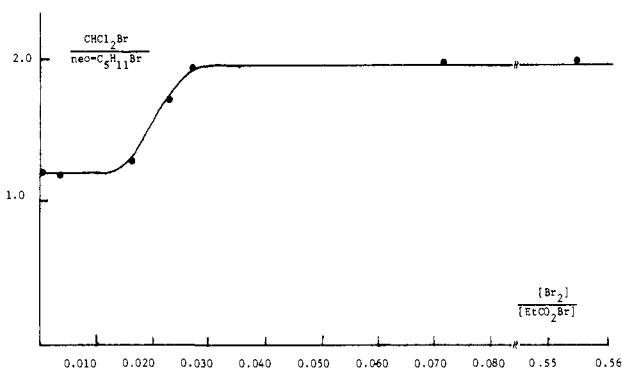
1-bromobutane, M	yields <sup>b</sup> dibromobutanes					remaining <sup>e</sup> EtCO <sub>2</sub> Br	S <sup>c</sup>	A <sup>d</sup>
	EtBr	1, 1	1, 2	1, 3	1, 4			
4.67	20	8.4	8.4	8.1	0.8	50%	1, 1, (1), 0.1	95 <sup>a</sup>
1.53	90	2.8	2.8	2.7	0.28	0	1, 1, (1), 0.1	99 <sup>f</sup>

<sup>a</sup> Irradiated 6 h with medium-pressure mercury arc through an interference filter (20 nm bandwidth for 50% of maximum transmission).  
<sup>b</sup>  $100 \times (\text{mmol of product}/\text{mmol of EtCO}_2\text{Br}_{\text{Initial}})$ . <sup>c</sup> (mmol of product/mmol of 1,3-dibromobutane). <sup>d</sup>  $100 \times (\text{mmol of brominated products} + \text{mmol of EtCO}_2\text{Br}_{\text{remaining}})/\text{mmol of EtCO}_2\text{Br}_{\text{Initial}}$ . <sup>e</sup> Reaction is slow due to the very low intensity of the light source.  
<sup>f</sup> Unfiltered medium pressure mercury arc, 15 min.

Table V. Reactions of Propionyl Hypobromite/Vinylidene Chloride with Methylene Chloride/Neopentane at  $-78^{\circ}\text{C}$ : Effect of Vinylidene Chloride Concentration

vinylidene <sup>c</sup> chloride	yields <sup>b</sup>				S <sup>e</sup>	A <sup>f</sup>
	EtBr	CHCl <sub>2</sub> Br	neo-C <sub>5</sub> H <sub>11</sub> Br	BrHC=CCl <sub>2</sub>		
0.024	88	4.08	3.54	<0.5 <sup>d</sup>	7.0	97
0.24	88	4.08	3.51	<0.5 <sup>d</sup>	7.0	97
0.59	88	3.92	3.39	0.54	6.9	96
3.6	86	3.77	3.18	4.5	7.1	98

<sup>a</sup> 0.260 mmol of EtCO<sub>2</sub>Br in 5 mL of Freon; 10 mmol each of CH<sub>2</sub>Cl<sub>2</sub> and neo-C<sub>5</sub>H<sub>11</sub>. <sup>b</sup>  $100 \times (\text{mmol of product}/\text{mmol of EtCO}_2\text{Br})$ . <sup>c</sup> Molarity. <sup>d</sup> Detection limit  $5 \times 10^{-4}$  mmol for this product. <sup>e</sup> (mmol of CHCl<sub>2</sub>Br/mmol of neo-C<sub>5</sub>H<sub>11</sub>Br)  $\times 6$ .  
<sup>f</sup>  $100 \times (\text{mmol of EtBr} + \text{mmol of CHCl}_2\text{Br} + \text{mmol of neo-C}_5\text{H}_{11}\text{Br})/\text{mmol of EtCO}_2\text{Br}$ .

Figure 1. Effect of bromine concentration on the reactions of propionyl hypobromite/bromine with methylene chloride/neopentane at  $-78^{\circ}\text{C}$ .

bromide as a function of the ratio of the concentrations of bromine to propionyl hypobromite. At ratios less than 0.02 the selectivity is the same as that observed in the presence of vinylidene chloride. As the ratio of  $[\text{Br}_2]/[\text{EtCO}_2\text{Br}]$  increases, the ratio of  $\text{CHCl}_2\text{Br}/\text{neo-C}_5\text{H}_{11}\text{Br}$  also increases and reaches a constant value of 2.0, which is invariant over a 20-fold change in ratio of reagents ( $[\text{Br}_2] = 0.0005\text{--}0.10\text{ M}$ ). Thus, method I conditions are attained if  $[\text{Br}_2]/[\text{EtCO}_2\text{Br}]$  is greater than 0.025.

Table VI. Reactions of Propionyl Hypobromite/Bromine with Methylene Chloride/Neopentane at  $-78^{\circ}\text{C}$ : Effect of Bromine Concentration<sup>a</sup>

[Br <sub>2</sub> ]	[Br <sub>2</sub> ]/[EtCO <sub>2</sub> Br]	yields <sup>b</sup>			CHCl <sub>2</sub> Br		S <sup>d</sup>	A <sup>e</sup>
		EtBr	CHCl <sub>2</sub> Br	neo-C <sub>5</sub> H <sub>11</sub> Br	neo-C <sub>5</sub> H <sub>11</sub> Br			
0 <sup>c</sup>	0	92	2.31	1.93	1.20	7.20	96	
0.0007	0.004	93	2.21	1.85	1.19	7.14	97	
0.0029	0.016	92	2.14	1.76	1.24	7.44	96	
0.0043	0.024	90	2.32	1.32	1.76	10.6	94	
0.0057	0.032	92	2.46	1.26	1.95	11.7	96	
0.013	0.071	92	2.39	1.20	1.99	11.9	96	
0.100	0.560	91	2.43	1.22	1.99	11.9	95	

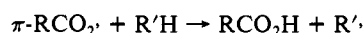
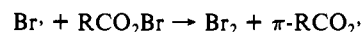
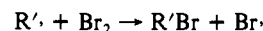
<sup>a</sup> Reaction composition: initially 0.880 mmol of EtCO<sub>2</sub>Br in 5 mL of Freon 11 containing 10 mmol each of CH<sub>2</sub>Cl<sub>2</sub> and neo-C<sub>5</sub>H<sub>11</sub>.  
<sup>b</sup>  $100 \times (\text{mmol of product}/\text{mmol of EtCO}_2\text{Br})$ . Yields determined by GC employing an internal standard. Excess Br<sub>2</sub> was removed by the addition of 1 mL of vinylidene chloride prior to analysis. <sup>c</sup> In the presence of 0.050 mL of vinylidene chloride. <sup>d</sup> (mmol of CHCl<sub>2</sub>Br/mmol of neo-C<sub>5</sub>H<sub>11</sub>Br)  $\times 6$ . <sup>e</sup>  $100 \times (\text{mmol of EtBr} + \text{mmol of CHCl}_2\text{Br} + \text{mmol of neo-C}_5\text{H}_{11}\text{Br})/\text{mmol of EtCO}_2\text{Br}$ .

### Mechanisms: Methods I and II

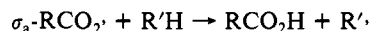
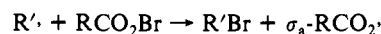
The invariance of selectivity observed with concentration changes of VC or Br<sub>2</sub>, outside of the crossover region, indicates that methods I and II can provide limiting conditions, the reagents setting up different reactions for generating carboxylate radical, and that within each of these two different regimes a single chain carrier is operating, labeled as C<sub>x</sub> for method I and C<sub>σ</sub> for method II. Alkyl radicals are trapped by molecular bromine in the method

#### Substitution Chain Steps

##### Method I

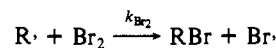
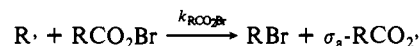


##### Method II



I regime and by acyl hypobromite in the method II regime.

**Absolute Rate Constant for Trapping of  $\cdot\text{CHCl}_2$  and neo-C<sub>5</sub>H<sub>11</sub> Radicals by Propionyl Hypobromite.** From the data summarized in Figure 1, a value of the absolute rate constant for radical trapping by EtCO<sub>2</sub>Br can be estimated. A ratio of CHCl<sub>2</sub>Br/neo-C<sub>5</sub>H<sub>11</sub>Br of 1.6 is intermediate to that observed in pure C<sub>x</sub> and pure C<sub>σ</sub> reactions. At this point, hydrogen abstractions must be occurring with approximately equal numbers of C<sub>x</sub> and C<sub>σ</sub> radicals. This can only occur when radicals are being trapped at the same rates by Br<sub>2</sub> and EtCO<sub>2</sub>Br, thus generating equal numbers of C<sub>x</sub> and C<sub>σ</sub> radicals. This occurs at a ratio of



$$k_{\text{Br}_2}[\text{Br}_2] = k_{\text{EtCO}_2\text{Br}}[\text{EtCO}_2\text{Br}]$$

$[\text{Br}_2]/[\text{EtCO}_2\text{Br}] = 0.020$ . On the assumption of an encounter-controlled rate constant for radical trapping by Br<sub>2</sub>,  $k_{\text{Br}_2} = 3 \times 10^{10}\text{ L}/(\text{mol s})$  at  $-78^{\circ}\text{C}$  in CCl<sub>3</sub>F,<sup>22</sup> the rate constant at

Table VII. Reactions of Propionyl Hypobromite/Bromine<sup>a</sup> with Butane at -78 °C (C<sub>π</sub>)

<i>n</i> -C <sub>4</sub> H <sub>10</sub> <sup>c</sup>	yields <sup>d</sup>			<i>S</i> <sup>e</sup>	<i>A</i> <sup>f</sup>
	EtBr	2-bromobutane	1-bromobutane		
1.08	94	4.11	0.363	17.6	98
1.37	93	5.23	0.457	17.2	99
2.09	90	7.34	0.677	16.3	98
6.20	75	20.1	1.97	15.3	97
				av 16.6	

<sup>a</sup> Typical reaction conditions: 5 mL of Freon solution containing 0.250 mmol of propionyl hypobromite and 0.01 mmol of Br<sub>2</sub> degassed prior to reaction. <sup>b</sup> Typical reaction conditions: 5 mL of Freon solution containing 0.250 mmol of propionyl hypobromite and 0.62 mmol of vinylidene chloride, degassed prior to reaction. <sup>c</sup> Molarities. <sup>d</sup> (mmol of product/mmol of propionyl hypobromite) × 100. <sup>e</sup> (mmol of 2-bromobutane/mmol of 1-bromobutane) × 6 primary hydrogens/4 secondary hydrogens. <sup>f</sup> (sum of mmol of all brominated products, including Hunsdiecker)/mmol of propionyl hypobromite) × 100.

Table VIII.<sup>a</sup> Reactions of Propionyl Hypobromite/VC<sup>b</sup> with Butane at -78 °C (C<sub>σ<sub>a</sub></sub>)

<i>n</i> -C <sub>4</sub> H <sub>10</sub> <sup>c</sup>	yields <sup>d</sup>			<i>S</i> <sup>e</sup>	<i>A</i> <sup>f</sup>
	EtBr	2-bromobutane	1-bromobutane		
0.83	97	1.44	0.258	9.3	99
1.08	95	1.95	0.332	8.8	97
1.60	93	2.93	0.495	8.9	96
2.09	92	3.65	0.645	8.5	96
				av 8.9	

<sup>a</sup> Footnotes as indicated under Table VII.

-78 °C for radical trapping by EtCO<sub>2</sub>Br is  $k_{\text{EtCO}_2\text{Br}} = 6 \times 10^8$  L/(mol s).

**Substrates Examined. Effect of Changing Substrate Concentration. Insensitivity to Change of R in RCO<sub>2</sub>Br.** The effect of changes in the concentration of substrate on the absolute yields of hydrogen-abstraction products, as well as Hunsdiecker products from decarboxylation, from, for example, the reactions of EtCO<sub>2</sub>Br/Br<sub>2</sub> (C<sub>π</sub>) at C-1 and C-2 of butane are given in Table VII and Figure 2a. An increase in the concentration of butane increases the yields of 1- and 2-bromobutane and decreases the yields of decarboxylation products, ethyl bromide and carbon dioxide. The selectivity of propionyloxy generated under these conditions does not change with changing substrate concentration.

Table VIII and Figure 2b show the analogous results under halogen-scavenging conditions (C<sub>σ<sub>a</sub></sub>). The yields of 1- and 2-bromobutane increase with increasing concentration of butane, and the yields of ethyl bromide and carbon dioxide decrease. Again, the selectivity is unaffected by changes in the concentrations of substrates. The constancy of these two selectivities indicates that there is no interconversion between C<sub>π</sub> and C<sub>σ<sub>a</sub></sub> in these experiments.

Analogous results were obtained with a wide spectrum of substrates, methylene chloride, chloroform, neopentane, butane, isobutane, and 1-bromobutane. Hydrogen atom abstraction competition reactions involving C<sub>π</sub> and C<sub>σ<sub>a</sub></sub> acetoxyl, propionyloxy, isobutyroxy, and pivaloxy were carried out over a wide range of substrate concentrations, typically, 1–5 M. Three to five reactions at different substrate concentrations were run for each carboxylate radical and plots similar to Figure 2a,b were obtained.<sup>45</sup> These selectivities and yields of substitution product at 5 M substrates for the 36 different types of competition reactions are summarized in Table IX. *The selectivities are the same for all C<sub>σ<sub>a</sub></sub>, regardless of the R in RCO<sub>2</sub>. Similarly, the selectivities of all C<sub>π</sub> are the same, again independent of R. In none of these cases is there any indication of interconversion of C<sub>π</sub> and C<sub>σ<sub>a</sub></sub>.*

**The Nature of Hydrogen Abstractions by Carboxylate Radicals.** Three criteria are used to probe the characteristics of hydrogen

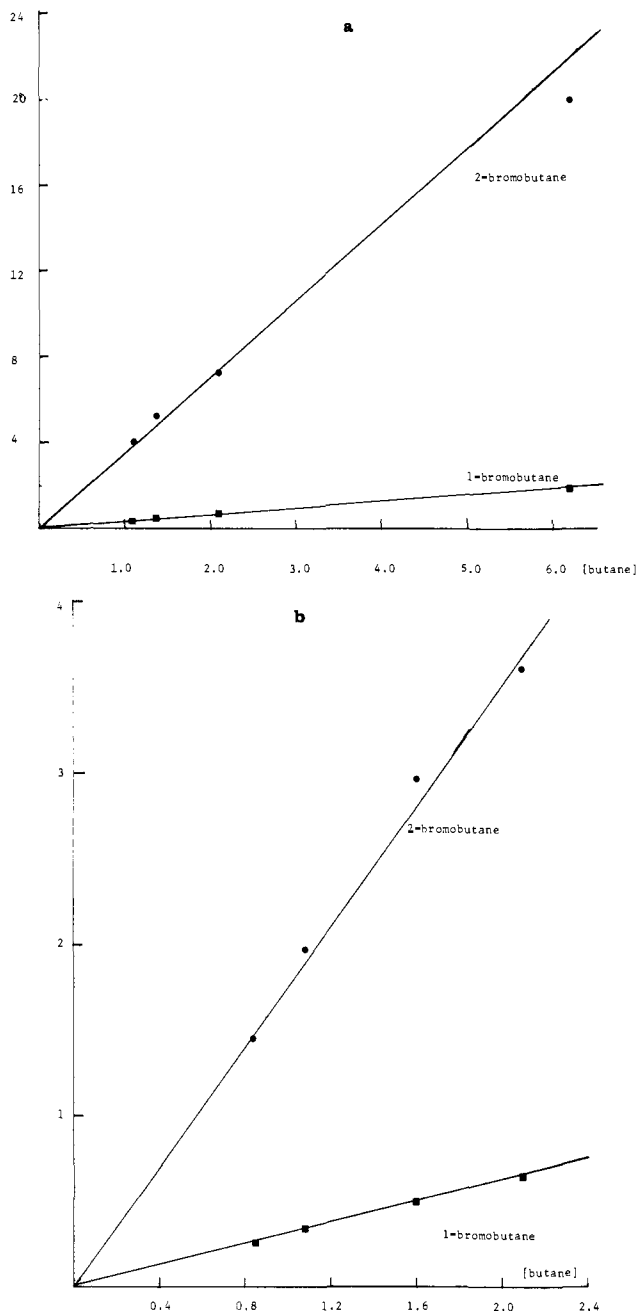


Figure 2. Percentage yields of 1- and 2-bromobutane as a function of butane concentration from the reactions of (a)  $\pi$ -propionyloxy at -78 °C and (b)  $\sigma_a$ -propionyloxy at -78 °C.

abstraction by carboxylate radicals, (1) sensitivity to bond strengths, (2) influence of the polar effect,<sup>23</sup> and (3) operation of an anchimeric effect.<sup>24</sup>

Relative rates of hydrogen abstraction by C<sub>π</sub> and C<sub>σ<sub>a</sub></sub> from primary, secondary, and tertiary carbon-hydrogen bonds are compared to the relative rates for other radicals in Table X, the ordering being from the least selective, Cl·, to the most selective, Br·. The reactivities of the carboxylate radicals toward aliphatic hydrogens approximate those of the succinimidyl radicals. The carboxylates are slightly less selective than the other oxygen-centered radicals, ·OH and *t*-BuO·. This low selectivity is indicative of hydrogen abstractions showing small sensitivity to the strengths of the attacked carbon-hydrogen bonds. These radicals abstract hydrogen with early transition states; there is little bond breaking for the substrate.

(23) Russell, G. A. In "Free Radicals"; Kochi, J. K., Ed.; Wiley-Interscience: New York, 1973; Vol. I, pp 275–332.

(24) Skell, P. S.; Shea, K. J. In "Free Radicals"; Kochi, J. K., Ed.; Wiley-Interscience: New York, 1973; Vol. II, pp 809–852.

(22) Calculated from  $k = 8RT/3000\eta$ . The value of  $\eta$  for CCl<sub>3</sub>F at -78 °C was estimated to be 0.0015 P by extrapolation of the data from: Badykies, I. S.; Kholod, T. K. 1960.

Table IX. Selectivities and Product Yields from Carboxylate-Radical-Mediated Brominations Employing Method I and II Conditions

carboxylate radical	CH <sub>2</sub> Cl <sub>2</sub> / <i>neo</i> -C <sub>5</sub> H <sub>12</sub>		CHCl <sub>3</sub> / CH <sub>2</sub> Cl <sub>2</sub>		1-bromobutane, S <sup>a</sup>					isobutane		<i>n</i> -butane	
	S <sup>a</sup>	Y <sup>b</sup>	S <sup>a</sup>	Y <sup>b</sup>	1,1	1,2	1,3	1,4	Y <sup>b</sup>	S <sup>a</sup>	Y <sup>b</sup>	S <sup>a</sup>	Y <sup>b</sup>
Method I (C <sub>π</sub> )													
MeCO <sub>2</sub>	11.9	20			1.0	1.0	(1)	0.10	25	104	39	17	18
EtCO <sub>2</sub>	12.7	20	3.8	46	1.0	1.0	(1)	0.10	27	98	31	17	19
<i>i</i> -PrCO <sub>2</sub>	12.3	30	3.8	55	1.0	0.99	(1)	0.09	36	90	42	20	27
<i>t</i> -BuCO <sub>2</sub>	12.6	73	3.6	60	0.99	1.0	(1)	0.09	44			21	56
Method II (C <sub>σ<sub>a</sub></sub> )													
MeCO <sub>2</sub>	7.4	21			0.59	0.62	(1)	0.20	24	46	18	9.1	12
EtCO <sub>2</sub>	6.9	21	2.5	33	0.67	0.64	(1)	0.20	26	45	15	8.9	9.9
<i>i</i> -PrCO <sub>2</sub>	7.1	28	2.5	36	0.59	0.60	(1)	0.19	28	46	21	9.1	19
<i>t</i> -BuCO <sub>2</sub>	6.6	73	2.5	46	0.54	0.54	(1)	0.25	52			9.9	35

<sup>a</sup> Selectivities, on a per-hydrogen basis. <sup>b</sup> Total substitution yield for all possible monobrominated products based on 5 M in each substrate, obtained from plots such as Figure 3a,b, the remainder being Hunsdiecker product. For 1-bromobutane this is the total for the dibromides.

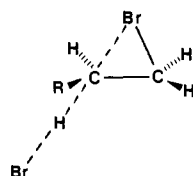
Table X. Relative Rates of Hydrogen Atom Abstraction from Aliphatic Carbon-Hydrogen Bonds<sup>a</sup>

radical	temp, °C	phase	1° H	2° H	3° H	ref
Cl·	-78	gas	(1)	6	12	26, 27
S <sub>σ</sub>	15	liquid	(1)	3.5	14.1	13
C <sub>σ<sub>a</sub></sub>	-78	liquid	(1)	10	45	<i>c</i>
C <sub>π</sub>	-78	liquid	(1)	20	90	<i>c</i>
S <sub>π</sub>	15	liquid	(1)	12	291	13
·OH	-78	gas	(1)	43	213	28
<i>t</i> -BuO·	-78	gas	(1)	45	2300	29
Me·	-78	gas	(1)	200	13000	14, 15
Et·	-78	gas	(1)	350	39000	16
Br·	-78	gas	(1)	18000	10 <sup>7</sup>	17
BDE <sup>b</sup>						
			98	95	92	

<sup>a</sup> Per-hydrogen basis. <sup>b</sup> BDE of carbon-hydrogen bonds, in kcal/mol, from ref 25a. <sup>c</sup> This work.

The intermolecular competitions with MC/N and C/MC mixtures indicate a smaller polar effect for carboxylate radicals than is shown by Cl· and S<sub>σ</sub> (Table XI). The polar effects on the transition states for H abstractions of the carboxylates and *t*-BuO· radical are similar and small. The difference between these oxygen-centered radicals and Cl· correlates satisfactorily with electron affinity values.

Competitive hydrogen abstraction from 1-bromobutane can identify involvement of the anchimeric effect.<sup>24</sup> The anchimeric effect is observed in reactions proceeding through late transition states, with extensive C-H bond breaking. Substituents such as an adjacent bromine lower the activation energy of this transition state and thus assist in the removal of a β-hydrogen; this leads to enhanced reactivity at that site. The effect can be recognized



by measuring the relative rates of hydrogen abstraction from the 2- and 3-position of 1-bromobutane. Although these positions both have secondary hydrogen atoms, in the absence of any anchimeric effect the 2 position would be deactivated by the polar effect. Thus, observation of increased reactivity at position 2 relative to 3 is an unambiguous indicator of an anchimeric effect.

The data in Table XII are ordered with increasing 1,2-/1,3-dibromobutane ratios. Anchimeric assistance begins to be evident with S<sub>σ</sub> and increases in the order S<sub>σ</sub> < C<sub>π</sub> < Br. This increasing dependence on assistance from a neighboring group suggests progressively less favorable hydrogen-abstraction energetics and more substrate bond breaking in the transition states.

Table XI. Relative Rates of Hydrogen Abstraction from CH<sub>2</sub>Cl<sub>2</sub>/*neo*-C<sub>5</sub>H<sub>12</sub> and CHCl<sub>3</sub>/CH<sub>2</sub>Cl<sub>2</sub> Mixtures<sup>a</sup>

radical	temp	phase	CH <sub>2</sub> Cl <sub>2</sub> / <i>neo</i> -C <sub>5</sub> H <sub>12</sub> <sup>d</sup>	CHCl <sub>3</sub> / CH <sub>2</sub> Cl <sub>2</sub> <sup>d</sup>	EA <sup>b</sup>
Cl·	-78	gas	0.004 <sup>27,30</sup>	0.21 <sup>30,31</sup>	83.2
S <sub>σ</sub>	+15	liquid	0.06 <sup>13</sup>	0.24 <sup>34</sup>	
S <sub>π</sub>	+15	liquid	1 <sup>13</sup>	2.14 <sup>34</sup>	
<i>t</i> -BuO·	0	liquid	10 <sup>29,32</sup>	4 <sup>32</sup>	43.1 <sup>e</sup>
C <sub>σ<sub>a</sub></sub>	-78	liquid	7.2 <sup>c</sup>	2.5 <sup>c</sup>	
C <sub>π</sub>	-78	liquid	12 <sup>c</sup>	3.8 <sup>c</sup>	
Me·	-78	gas	2300 <sup>14,33</sup>	23 <sup>33</sup>	24.8
Br·	+15	liquid	15.5 <sup>34</sup>	0.85 <sup>34</sup>	77.4

<sup>a</sup> Per-hydrogen basis. <sup>b</sup> Electron affinities in kcal/mol from ref 25d. <sup>c</sup> This work. <sup>d</sup> BDE (kcal/mol: *neo*-C<sub>5</sub>H<sub>12</sub>, 100.3;<sup>25a</sup> CHCl<sub>3</sub>-H, 99;<sup>25d</sup> CCl<sub>3</sub>-H, 95.7<sup>25c</sup>). <sup>e</sup> Reference 25f.

Table XII. Relative Rates of Hydrogen Abstraction from 1-Bromobutane<sup>a</sup>

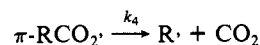
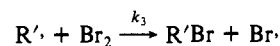
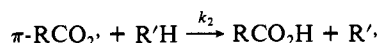
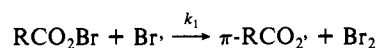
reagent	radical	temp, °C	BrCH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>3</sub>			ref	
Cl <sub>2</sub>	Cl·	60	0.093	0.434	(1.0)	0.455	36
NBS/olefin	S <sub>σ</sub>	15	0.20	0.54	(1.0)	0.43	13
MeCO <sub>2</sub> Br/VC	C <sub>σ<sub>a</sub></sub>	-78	0.60	0.60	(1.0)	0.20	<i>b</i>
<i>t</i> -BuOBr	<i>t</i> -BuO·	45	0.64	0.77	(1.0)	0.15	13a
MeCO <sub>2</sub> Br/Br <sub>2</sub>	C <sub>π</sub>	-78	1.0	1.0	(1.0)	0.1	<i>b</i>
NBS/CCl <sub>3</sub> Br	S <sub>π</sub>	15	0.11	2.41	(1.0)	0.19	13
Br <sub>2</sub>	Br·	60	0.062	5.78	(1.0)	0	36
Br <sub>2</sub>	Br·	-78		160	(1.0)		<i>c</i>

<sup>a</sup> Liquid phase. Rates normalized to the 3-position arbitrarily defined as unity on a per hydrogen basis. <sup>b</sup> This work. <sup>c</sup> Extrapolated from data in ref 35.

The effect on the reactivity at C-1 is intriguing, and we are attempting to extend our understanding of this polar effect by further work along this line.

#### Free Radical Chains That Produce Carboxylate Radical.

##### Method I (bromine containing)



##### Method II (bromine scavenged)

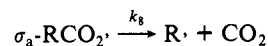
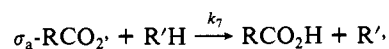
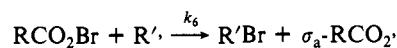


Table XIII. Relative Rate Constants of Decarboxylation/Hydrogen Abstraction from Butane by  $\pi$ - and  $\sigma_a$ -RCO<sub>2</sub> at -78 °C<sup>a</sup>

radical	$k_d/k_2$ (1°)	$k_d/k_2$ (2°)
$\pi$ -propionyxy	295	25.1
$\pi$ -isobutyroxy	217	15.4
$\pi$ -pivaloxy	72.2	4.70
	$k_8/k_7$ (1°)	$k_8/k_7$ (2°)
$\sigma_a$ -propionyxy	322	56.2
$\sigma_a$ -isobutyroxy	181	27.7
$\sigma_a$ -pivaloxy	89.4	12.1

<sup>a</sup> Values obtained from a least-squares treatment of data of the type displayed in Figure 2a, 2b;  $r = 0.97$ -1.00.

The full chain sequences are designed to delineate the rationale for (a) producing two unique hydrogen abstractors in different experimental regimes, independent of the concentrations of Br<sub>2</sub> or VC, and (b) the effect of substrate concentration in determining the distributions between substitution and decarboxylation.

Method I employs a three-step chain sequence for substitutions, method II a two-step sequence. For both carboxylate radicals, a first-order decarboxylation, leading to the Hunsdiecker product, is shown in competition with second-order hydrogen abstraction from substrate.

**Kinetic Analysis.** The quantitative dependence of the ratio (Hunsdiecker product/hydrogen abstraction product) on substrate concentration can be derived from the chains steps shown above and the steady-state approximation. At 100% conversion of acyl hypobromite, in the presence of excess substrates:

Method I

$$\frac{(\text{RCO}_2\text{Br})_i}{(\text{R}'\text{Br})_f} - 1 = \frac{k_4}{k_2[\text{R}'\text{H}]}$$

Method II

$$\frac{(\text{RCO}_2\text{Br})_i}{(\text{R}'\text{Br})_f} - 1 = \frac{k_8}{k_7[\text{R}'\text{H}]}$$

This treatment predicts a linear plot of the left-hand side of the equations against  $[\text{R}'\text{H}]^{-1}$ , going through the origin, with slopes  $k_4/k_2$  and  $k_8/k_7$ , respectively.

All of the data summarized in Table IX (and reported in detail)<sup>45</sup> are consistent with this treatment, as illustrated in Figure 3a,b for  $\pi$ - and  $\sigma_a$ -propionyxy. This supports the hypothesis that under method I ( $C_\pi$ ) or method II ( $C_{\sigma_a}$ ) regimes, the slow steps are second-order hydrogen abstractions from substrates,  $k_2$  or  $k_7$ , and first-order decarboxylations,  $k_4$  or  $k_8$ , both processes depending on the same intermediate. The slopes of these lines are the ratios of rate constants for decarboxylation divided by H abstractions ( $k_d/k_a$ ) (Table XIII).

Since these plots go through the origin, it follows that at infinite alkane concentration the decarboxylation route would be eliminated. Consequently, the hydrogen abstractors are the only intermediates that produce carbon dioxide. *Two hydrogen abstractors are required, each of which is in a direct line to independent channels that lead to carbon dioxide.*

This decrease in  $k_d/k_a$  values with change in R from Et to *i*-Pr to *t*-Bu in both the  $C_\pi$  or  $C_{\sigma_a}$  series cannot be attributed to changes in  $k_a$ .<sup>20</sup> Since the selectivities in hydrogen abstractions are invariant with change in R, it follows that  $k_a$  is similar for all  $C_\pi$  or  $C_{\sigma_a}$ . The changes in  $k_d/k_a$  with change in R is, therefore, attributed entirely to changes in  $k_d$ . It is concluded that the order of increasing rate of decarboxylation is pivaloxy < isobutyroxy < propionyxy. *These rates do not increase with increasing stability of the radical formed in this decarboxylation process.* The implications of this conclusion will be considered in detail in a subsequent publication.

**Ab Initio Calculations.** Peyerimhoff et al.<sup>10</sup> have carried out state-of-the-art ab initio calculations with full configuration interactions for both formoxy and acetoxy radicals. Both are similar: Within a span of 14 kcal there are three states for formoxy, a ground state, <sup>2</sup>B<sub>2</sub> (our  $C_{\sigma_a}$ ), and two close-lying upper states, <sup>2</sup>A<sub>2</sub>

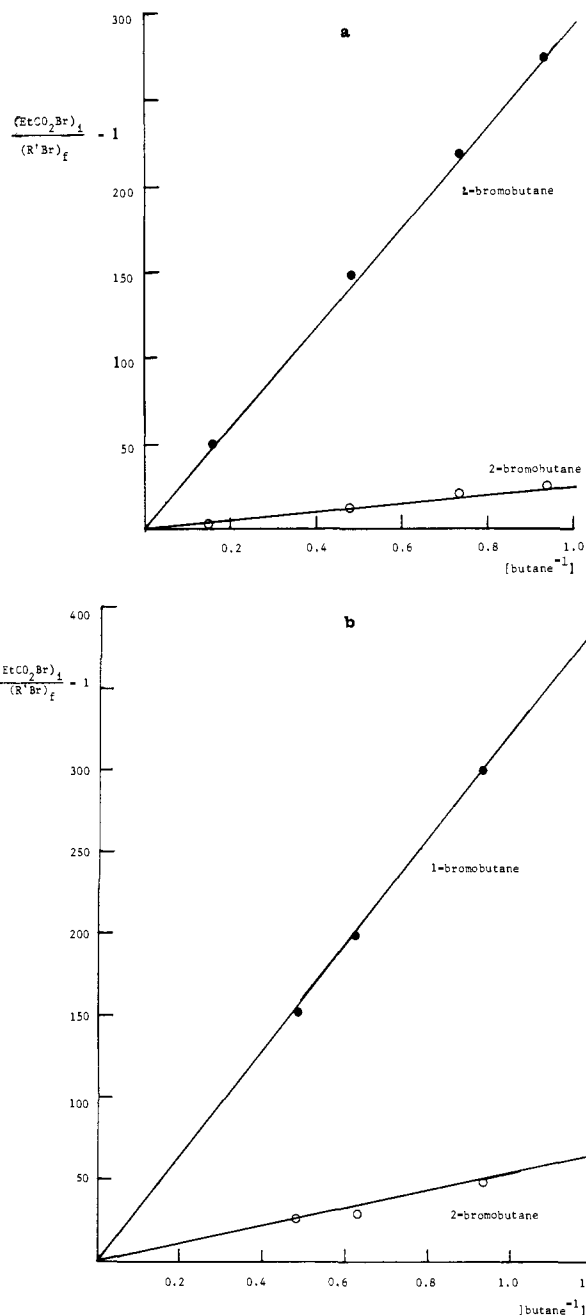
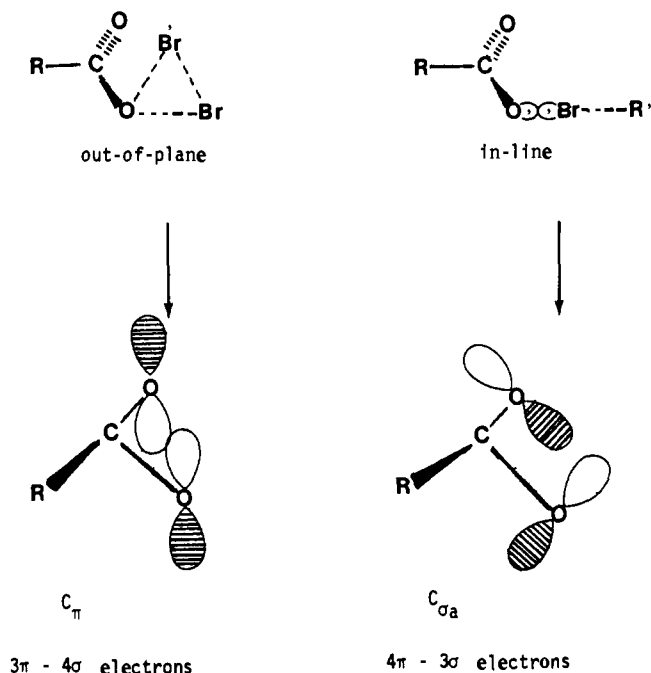


Figure 3.  $(\text{EtCO}_2\text{Br})_2/(\text{R}'\text{Br})_f - 1$  vs.  $[\text{butane}]^{-1}$  for the reactions of (a)  $\pi$ -propionyxy at -78 °C and (b)  $\sigma_a$ -propionyxy at -78 °C.

(our  $C_\pi$ ) and <sup>2</sup>A<sub>1</sub> (our label,  $C_{\sigma_a}$ ). The acetoxy state analogous to the <sup>2</sup>A<sub>1</sub> state has an equilibrium OCO angle of 135° and has no restoring barrier for stretching of the C-C bond; this state must lose carbon dioxide too rapidly to be a contributor to the substitution processes. The states analogous to formoxy <sup>2</sup>B<sub>2</sub> and <sup>2</sup>A<sub>2</sub> have OCO angles 112° and 122°, respectively, and have barriers to stretching the C-C bond. Thus these states can have lifetimes sufficient to account for the second-order hydrogen abstractions. As a minimum, these two states must be included in the kinetic scheme. The kinetic evidence neither requires nor can it exclude the involvement of  $C_{\sigma_a}$  as a third intermediate in a decarboxylation reaction channel. The data require only that  $C_{\sigma_a}$ , if it is an intermediate, is not produced directly but is produced from  $C_\pi$  or  $C_{\sigma_a}$  or from both.

While it is evident that theory describes two suitable states and the experiments require two states, the arguments for the correlation of these states is not strong. We assign the <sup>2</sup>B<sub>2</sub> type state to our method II state,  $C_{\sigma_a}$ , and that leaves the <sup>2</sup>A<sub>2</sub> type state for our method I state,  $C_\pi$ . The opposite might be correct! We make this correlation by analogy with the succinimidylyls<sup>13</sup> on the fol-

Scheme I



lowing basis: bromine atom reacts with NBS (method I) to make the  $S_{\pi}$ ; alkyl radical plus NBS (method II) makes  $S_{\sigma}$ .

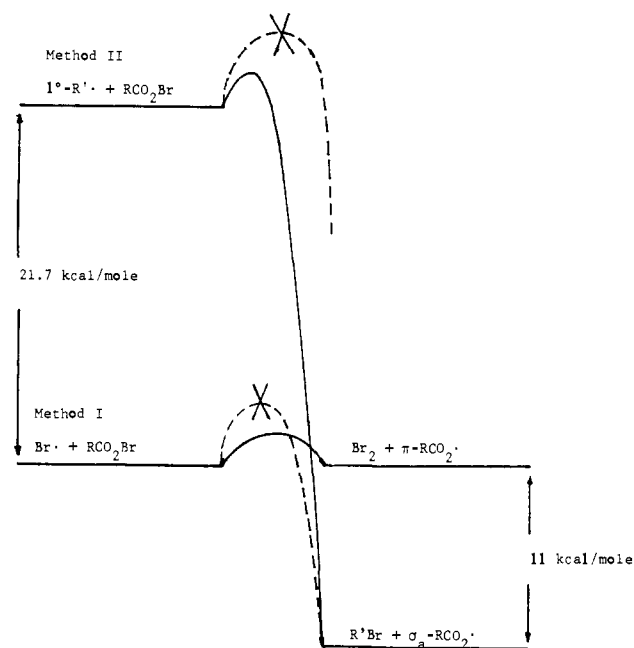
A useful transition-state hypothesis in succinimidyl chemistry is that Br $\cdot$  approaches NBS from above the plane of the molecule and alkyl radical approaches in alignment with the Br-N bond. These transition-state descriptions receive support from the calculations reported by Clark.<sup>37</sup> Electrophilic radicals prefer an above-plane approach, nucleophilic an in-line approach.

Thus we propose method I leads to  $C_{\pi}$  via an above-plane approach of Br $\cdot$  to the acyl hypobromite, and method II leads to  $C_{\sigma_a}$  via an in-line approach of R $\cdot$ , in alignment with the O-Br bond, as illustrated in Scheme I.

**Radical-Generating Bond Energetics.** Thermodynamic data for the acyl hypobromites are not available in the desired form. Analysis of the vibration spectrum of acetyl hypochlorite leads to an O-Cl bond energy of 55 kcal/mol,<sup>38</sup> very close to the Cl<sub>2</sub> BDE (56 kcal/mol).<sup>25e</sup> It is not unreasonable to assign to the O-Br BDE of the acyl hypobromites the same value as the BDE of Br<sub>2</sub> (46 kcal/mol).<sup>25e</sup> With this value, the assignment of  $C_{\pi}$  to method I conditions, and the 11 kcal/mol calculated for  $C_{\pi}$  and  $C_{\sigma_a}$  separation for acetoxy, an energy diagram can be constructed (see Chart I).

The choice of reaction channels by these reactants is remarkable and could not have been predicted from energy considerations alone. A strong bias for different transition states in the paths to  $C_{\pi}$  and  $C_{\sigma_a}$  is evident, and this makes more urgent the con-

Chart I



sideration of factors such as those proposed by Clark.<sup>37</sup>

### Experimental Section

**General.** <sup>1</sup>H NMR spectra were recorded on a 60-MHz spectrometer with chemical shifts reported on the  $\delta$  scale relative to Me<sub>4</sub>Si. IR spectra were recorded on a grating spectrometer with a polystyrene standard. Gas chromatographic (GC) analyses of reaction mixtures were carried out subsequent to the addition of an internal standard and 1 mL of vinylidene chloride to react with free bromine. A FID detector fitted with a 6 ft  $\times$  2 mm glass 1% Carbowax on 60/80 graphitized carbon was used for all analyses except for dibromobutane, which employed a 6 ft  $\times$  2 mm glass 10% cyanopropyl silicone gum on 100/120 silanized firebrick. Products were identified by GC retention times and quantitated by measuring peak heights and employing sensitivity factors as determined with authentic samples. Carbon dioxide yields were determined by a trap-to-trap distillation at 10 mmHg through a -130 (pentane/N<sub>2</sub>(l)) -196 and °C a trap. The contents of the -196 °C trap were measured volumetrically and analyzed by GC with thermal-conductivity detector with 30 ft  $\times$  0.25 in. 20% hexanedione on 60/80 firebrick. All glassware used with the acyl hypobromites was flame or oven dried prior to use. Syntheses and transfer of the acyl hypobromites was carried out in a dark hood.

**Materials.** Trichlorofluoromethane and methylene chloride were each purified by successive extraction with concentrated sulfuric acid and 5% sodium bicarbonate; chloroform was extracted with concentrated phosphoric acid, and all three solvents were further extracted with distilled water, dried over anhydrous calcium chloride, and distilled from phosphorus pentoxide. The purified solvents were stored over 4-Å molecular sieves. Chlorine was dissolved in CCl<sub>4</sub>F and stored over molecular sieve; chlorine content was determined iodometrically. All chemicals were >99% purity. Vinylidene chloride was freed from inhibitors by distillation in vacuum.

**1,2-Dibromo-2,2-dichloroethane.** To 0.25 mol of vinylidene chloride in 50 mL of CCl<sub>4</sub>F in a water cooled bath at room temperature was added 0.25 mol of bromine over a period of 10 min with 100-W tungsten lamp irradiation. The reaction mixture was distilled and a fraction boiling at 63–65 °C (15 mmHg) was collected (90% yield) [lit.<sup>39</sup> bp 58.8 °C (10 mmHg)].

**1-Bromo-2,2-dichloroethane.** To 25 g of 1,2-dibromo-2,2-dichloroethane 1 was added 1 equiv of 10% ethanolic KOH over a period of 10 min. The flask was stirred an additional 10 min, after which 50 mL of water was added, and the organic layer was removed and dried with anhydrous magnesium sulfate. The resulting yellow oil was distilled at atmospheric pressure and the fraction boiling at 122–125 °C was collected (34% yield) [lit.<sup>40</sup> bp 107 °C (760 mmHg)]; IR (neat film,  $\mu$ m)

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3.24 (s), 6.26 (s), 8.12 (s), 11.0 (b), 12.9 (b), 13.4 (b) [lit.<sup>41</sup> IR (neat film,  $\mu\text{m}$ ) 3.25 (s), 6.4 (s), 8.2 (s), 11.1 (b), 13.1 (b), 13.4 (b)].

**1,1-Dibromobutane.** This material was prepared from the procedure outlined by Conly<sup>42</sup> using  $\alpha$ -bromo silver valerate and bromine. A liquid boiling at 90–91 °C (100 mmHg) was collected (42% yield) [lit.<sup>42</sup> bp 90.5–92 °C (101 mmHg)]; <sup>1</sup>H NMR (CCl<sub>4</sub>)  $\delta$  0.7–3.0 (m, 9 H), 5.63 ( $J = 6$  Hz, 1 H).

**Silver Salts.** The silver salts were prepared by neutralizing a 0.25 M aqueous solution of the parent acid with concentrated ammonium hydroxide. This solution was cooled to 0 °C and added to a 0.25 M aqueous solution at 0 °C, containing 1 equiv of silver nitrate, in a dark hood. After addition was complete, the solution was hand stirred for 5 min, and the white silver salt collected in a Büchner funnel, washed with water, and aspirator dried for 30 min. The silver salts were further dried under vacuum ( $p < 1 \mu\text{mHg}$ ,  $T = \text{ambient}$ ) overnight. Typically the yield of dry silver salt was 85–90% containing, according to Volhard titration,<sup>43</sup> 98–100% of the expected silver content.

**Acetyl Hypobromite and Propionyl Hypobromite.** To a stirred suspension of 5 mmol of the respective silver salt in CCl<sub>3</sub>F at 0 °C was added 0.26 mL (5.2 mmol) of bromine in 10 mL of CCl<sub>3</sub>F via dropping funnel over a period of 5 min under a blanket of nitrogen. After addition was complete, the mixture was stirred for an additional 10 min, producing a yellow-orange solution. The addition funnel was removed, the reaction flask was fitted with a coarse frit and Schlenk tube, and the contents were filtered under reduced pressure into a –23 °C bath (CCl<sub>4</sub>/dry ice). These acyl hypobromite/bromine solutions appear to be stable indefinitely in solution at –23 °C in a dark hood under a stream of nitrogen.

**Caution:** Removal of CCl<sub>3</sub>F at –23 °C from these solutions leaves white crystals of acetyl hypobromite or propionyl hypobromite in 50% yield. A spontaneous explosion occurred from ~1 g of dry propionyl hypobromite at –23 °C under a dynamic vacuum of <1 mmHg.

**Acetyl Hypochlorite.** To a stirred suspension of 5 mmol of silver acetate in 40 mL of CCl<sub>3</sub>F at 0 °C was added a CCl<sub>3</sub>F solution containing 1 equiv of chlorine via dropping funnel over a period of 5 min under a blanket of nitrogen. After addition was complete, the mixture was stirred an additional 30 min. The addition funnel was removed, the reaction flask was fitted with a coarse frit and Schlenk tube, and the contents were filtered under reduced pressure into a –23 °C bath. The resulting solution was concentrated to ~25 mL by removal of solvent under vacuum at –23 °C. This resulting solution was analyzed by the procedure for the acyl hypobromites.

**Isobutyryl Hypobromite.** To a stirred suspension of 5 mmol of silver isobutyrate in 90 mL of CCl<sub>3</sub>F at –41 °C (acetonitrile/dry ice) was added 0.26 mL (5.2 mmol) of bromine in 10 mL of CCl<sub>3</sub>F over a period of 5 min with a dropping funnel under a blanket of nitrogen. After addition was complete, the mixture was stirred for an additional 20 min to produce a yellow-orange solution. The addition funnel was removed and the reaction flask fitted with a coarse frit wrapped with dry ice and a Schlenk tube. The contents were filtered under reduced pressure into a –41 °C bath. The acyl hypobromite appeared to be stable at this temperature in a dark hood indefinitely.

**Pivaloyl Hypobromite.** Pivaloyl hypobromite was prepared from freshly prepared silver pivaloate and bromine by a method identical with that described for the synthesis of isobutyryl hypobromite except that the reactants were stirred for 2 h prior to filtration.

**Analysis of Acyl Hypobromite Solution.** The amounts of acyl hypobromite and bromine were determined by the following procedure:

A 5-mL aliquot of acyl hypobromite/bromine was added to acidic potassium iodide (1 g of KI/20 mL of 1 M HCl) and the liberated iodine was titrated with standardized sodium thiosulfate to determine moles of Br<sup>+</sup>.<sup>43</sup> Another 5-mL aliquot of acyl hypobromite/bromine was reduced with aqueous (0.1 M) sodium bisulfite. Excess bisulfite was destroyed with 1 M nitric acid and the resulting solution made slightly basic with 5% sodium bicarbonate. Bromide ion was then determined by silver nitrate titration with potassium chromate indicator (Mohr).<sup>43</sup> The amounts of acyl hypobromite and bromine can then be determined from the following set of equations:

$$\text{mmol of Br}^+ = N \text{ mmol of acyl hypobromite} + m \text{ mmol of bromine,}$$

$$\text{mmol of Br}^- = N \text{ mmol of acyl hypobromite} + 2m \text{ mmol of bromine,}$$

$$\text{mmol of Br}^- - \text{mmol of Br}^+ = m \text{ mmol of bromine,}$$

$$\text{mmol of Br}^+ - m \text{ mmol of bromine} = N \text{ mmol of acyl hypobromite}$$

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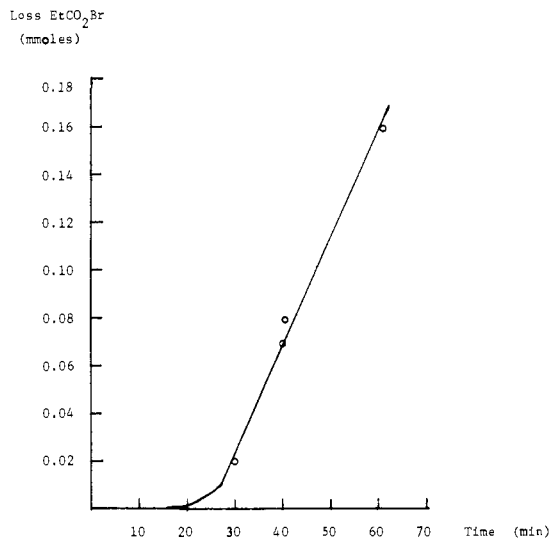


Figure 4. Loss of EtCO<sub>2</sub>Br as a function of time at –78 °C.

Typical preparations of all acyl hypobromites produced the desired acyl hypobromite in solution in greater than 95% yield based on silver salt. Irradiation of these degassed solutions at –78 °C produced the Hunsdiecker products (alkyl halide and carbon dioxide) in greater than 98% yield based on millimoles of acyl hypobromite.

**Typical Reactions: Methods I and II.** All reactions were carried out in 30-mL-capacity Pyrex pressure tubes fitted with Teflon needle valves. Standardized aliquots of acyl hypobromite/bromine in CCl<sub>3</sub>F were degassed three times by a freeze–thaw technique by freezing, evacuating at –196 °C ( $p \sim 0.01$  mmHg), and warming to the melting point of CCl<sub>3</sub>F (~–110 °C) in ambient light (fluorescent). Vinylidene chloride (method II reactions) was degassed and transferred by standard vacuum procedures to remove inhibitor. Reactants were measured, degassed, and transferred into these tubes by standard vacuum line techniques. The sealed pressure tube was placed into a Pyrex Dewar, maintained at –100 °C (ethyl ether/N<sub>2</sub>(l)), –78 °C (acetone/dry ice), and –63 °C (chloroform/dry ice) slush baths and irradiated with a 400-W medium-pressure mercury arc, approximately 6 in. away, for 15 min. These reaction mixtures were stirred with Teflon-coated magnetic stir bars. Products were analyzed as described earlier in the Experimental Section.

**Chain Lengths.** Quantum yield determinations were carried out with a Hanovia 100-W high-pressure mercury arc and a grating monochromator (bandwidth  $\pm 8.0$  nm). The intensity of the light source was standardized by potassium ferrioxalate actinometry following the procedure of Hatchard and Parker.<sup>44</sup> All reactions and standardizations were carried out in a 2-cm Pyrex cuvette, in which the reactants had been degassed and sealed off by a Teflon needle valve. The photolyses were effected at –78 °C (methanol/dry ice) in a quartz Dewar. The reaction course was followed by withdrawing the entire contents of the cuvette at convenient time intervals and determining the loss of propionyl hypobromite by direct titration of liberated iodine with standardized sodium thiosulfate. After an induction period of approximately 25 min, a linear plot of the loss of propionyl hypobromite vs. time was obtained. A representative plot of the loss of PHB vs. time with a standardized 313  $\pm 8.0$  nm light source of  $1.21 \times 10^{-7}$  einstein/min is shown in Figure 4. After subtracting out the induction time, the quantum yield was calculated as mmol of reacted EtCO<sub>2</sub>Br/mmol of photons.

**Acknowledgment.** We wish to thank the National Science Foundation for its financial support of this work.

**Registry No.** MeCO<sub>2</sub>Br, 4254-22-2; EtCO<sub>2</sub>Br, 82198-80-9; *i*-PrCO<sub>2</sub>Br, 82198-81-0; *t*-BuCO<sub>2</sub>Br, 82198-82-1; MeCO<sub>2</sub>Cl, 758-11-2; H<sub>2</sub>C=CCl<sub>2</sub>, 75-35-4;  $\cdot\text{CHCl}_2$ , 3474-12-2; *neo*-C<sub>5</sub>H<sub>11</sub>•, 3744-21-6; BrCH=CCl<sub>2</sub>,

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(47) Recently we have found that in an equal volume solution of CHCl<sub>3</sub>/CH<sub>2</sub>Cl<sub>2</sub> (6.2 and 7.8 M, respectively) addition of bromine to silver propionate at 25 °C produces 14% CBrCl<sub>3</sub> and 10% CHCl<sub>2</sub>Br, the remainder being Hunsdiecker product. Thus at 25 °C the per hydrogen selectivity is 3.5, nearly the same as at –78 °C (3.8), substantiating the small activation energies for hydrogen abstractions.

5870-61-1; Br<sub>2</sub>, 7726-95-6; Cl<sub>2</sub>, 7782-50-5; CH<sub>2</sub>Cl<sub>2</sub>, 75-09-2; *neo*-C<sub>4</sub>H<sub>12</sub>, 463-82-1; *n*-C<sub>4</sub>H<sub>10</sub>, 106-97-8; MeCO<sub>2</sub>, 13799-69-4; EtCO<sub>2</sub>, 24446-96-6; *i*-PrCO<sub>2</sub>, 54388-94-2; *t*-BuCO<sub>2</sub>, 28149-41-9; H, 12385-13-6; CHCl<sub>3</sub>, 67-66-3; 1,2-dibromo-2,2-dichloroethane, 75-81-0; 1,1-dibromobutane, 62168-25-6; silver acetate, 563-63-3; silver propionate, 5489-14-5; silver isobutyrate, 24418-71-1; silver pivaloate, 7324-58-5; 1-bromobutane,

109-65-9.

**Supplementary Material Available:** A listing of the results from reactions of all acyl hypobromites summarized in Table IX at various alkane concentrations (37 pages). Ordering information is given on any current masthead page.

## Vinyl Cations. 40. $\pi$ - and $\sigma$ -Routes to Vinyl Cations. Solvolyses of 2-Methylcyclohexenyl, Cyclopentylideneethyl, Hex-5-yn-1-yl, and Related Triflates<sup>1</sup>

Michael Hanack,\* Karl-Albrecht Fuchs, and Clair J. Collins\*<sup>2</sup>

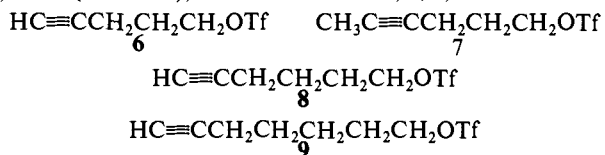
Contribution from the Institut für Organische Chemie, Lehrstuhl für Organische Chemie II der Universität Tübingen, D-7400 Tübingen 1, West Germany. Received November 15, 1982

**Abstract:** 2-Methylcyclohexenyl triflate (**1**), cyclopentylideneethyl triflate (**2**), and hept-6-yn-1-yl triflate (**3**) were solvolyzed at various temperatures in water-alcohol mixtures, in TFE-water mixtures, in TFA, in TFIP, in HFIP, and in 100% TFE in the presence of various buffers and the resulting products were determined. The three reactants were also solvolyzed in a standard mixture (1:100:100 = triflate:TFE:Na<sub>2</sub>CO<sub>3</sub>) at various temperatures, and the yields of products were compared. The solvolysis products were shown to be under kinetic control. Internal return occurs. From the foregoing data it is concluded that triflates **1** and **2** solvolyze through vinyl cation intermediates without  $\sigma$ -participation, whereas **3** solvolyzes through  $\pi$ -participation. The results of the solvolyses of **1** and **2** can be explained through classical cations that interchange through a transition state, **25**, but that never reach equilibrium. The cations exist as oriented ion pairs in which the counterion partially controls product formation. Triflate **3** solvolyzes in TFE-Na<sub>2</sub>CO<sub>3</sub> with anchimeric assistance, but there is no evidence for the bridged ion **25**. Four additional acyclic triflates (**6-9**), in which the triple bonds are three, four, and five carbons removed from the leaving group, were also solvolyzed and the results are discussed in terms of their mechanistic implications.

Vinyl cations<sup>3,4</sup> can be generated by heterolysis of vinyl esters<sup>4</sup> that contain appropriate leaving groups attached directly to the double bond, by the addition of electrophilic reagents to allenic or acetylenic bonds,<sup>4</sup> or by triple bond participation, as in the solvolysis of homopargyl<sup>2,5-9</sup> triflate.

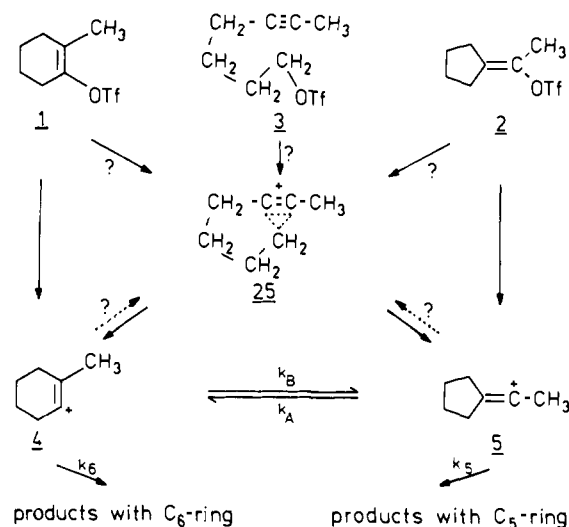
Just as with carbocations whose electron-deficient carbons are sp<sup>2</sup> hybridized, vinyl cations also rearrange<sup>4</sup> and exhibit internal return.<sup>4</sup> There is good evidence that nonclassical vinyl cations can exist, since cyclobutenyl nonaflate (nonafluorobutanesulfonate) solvolyzes 3720 times faster,<sup>10,11</sup> at 100 °C, than cyclohexenyl nonaflate. Cyclopentenyl nonaflate, under similar conditions, does not cleave its carbon-oxygen bond but instead undergoes a second-order solvolysis with oxygen-sulfur cleavage.<sup>12</sup>

We report here our results on the solvolyses of the triflates **1**, **2**, and **3** (Scheme I), as well as those of **6**, **7**, **8**, and **9**. Triflates



**1**, **2**, and **3** should all be converted to many of the same products,

Scheme I



although, as it turns out, not in the same proportions. The so-called "linear", secondary vinyl cation **5** is more stable<sup>4</sup> than the "bent" vinyl cation **4**, and consequently one might expect triflate **1**, in solvents of low nucleophilicity and high ionizing power, to exhibit considerable anchimeric assistance<sup>13</sup> through  $\sigma$ -participation. To the extent that triflate **2** rearranges to yield products containing six-carbon rings, anchimeric assistance is also conceivable. Further, triflate **3** cannot cyclize, during solvolysis, without  $\pi$ -participation of the triple bond, although the existence of such participation is not synonymous with nonclassical ions, or bridging, as has been pointed out by Winstein.<sup>14</sup>

(1) Portions of this manuscript are from the Ph.D. Dissertation of K.-A. Fuchs, Universität des Saarlandes, Saarbrücken, 1978.

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