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(4) For details of the procedures of data collection and data processing see W. M. Butler and J. H. Enemark, *Inorg. Chem.*, **13**, 540 (1973), and references therein.

(5) $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R_2 = [\Sigma w(F_o - F_c)^2/\Sigma wF_o^2]^{1/2}$.

(6) Final atomic parameters are available, see note at the end of this communication.

(7) If the bridging ligand were 2-mercaptoethanol itself rather than the 2-mercaptoethanolate dianion, then **2** would be a dimeric Mo(IV) complex. The similarity of the electronic spectrum of **2** to other dimeric oxomolybdenum(V) species[8] and the absence of O-H and S-H bands in the infrared spectrum of **2** support the Mo(V) formulation. Meaningful proton magnetic resonance spectra of **2** could not be obtained because of its low solubility in suitable solvents.

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John I. Gelder, John H. Enemark*
Department of Chemistry, University of Arizona
Tucson, Arizona 85721

G. Wolterman, D. A. Boston, G. P. Haight
Department of Chemistry, University of Illinois
Urbana, Illinois 61801

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Absolute Rate Constants for Reaction of the *tert*-Butylperoxy Radical with 1-Bromo-2-methylpropane and 1-Chloro-2-methylpropane. Kinetic Evidence for Anchimeric Assistance in the Abstraction of a β-Hydrogen Atom for Alkyl Bromides and Chlorides[1]

Sir:

A large amount of effort has been expended to prove[2] and disprove[3] the concept that H-atom transfer reactions can be accelerated by a β substituent via a bridged intermediate. Most of the experimental evidence has, however, been obtained from free radical brominations of alkyl bromides, reactions that may be complicated by the reversibility of the H-atom transfer reactions, and elimination of Br· from β-bromoalkyl radicals.[3]

Alkylperoxy radicals (ROO·) and the bromine atom have similar selectivities to H-atom transfer even though Br· is about 10^6 times more reactive.[4] An alkylperoxy radical should, therefore, be a better probe for anchimeric assistance because accurate rate constants for H-atom abstraction can easily be obtained at very low extents of reaction where the reaction can not be reversible.[5] Furthermore, complications due to β-scission of β-bromoalkyl radicals can be eliminated by performing the reaction in the presence of a substantial concentration of hydroperoxide (ROOH).[6]

In this communication we report the results of a kinetic study of the liquid-phase autoxidation of 1-bromo-2-methylpropane (**1**) and 1-chloro-2-methylpropane (**2**) at 30°. This work provides kinetic evidence in support of anchimeric assistance to H-atom transfer by β-chloro and β-bromo substituents.

Kinetic data for the autoxidation of **1** and **2** in the absence and presence of *tert*-butyl hydroperoxide are summarized in Table I. Overall rates of autoxidation ($-d[O_2]/dt$) were determined from the consumption of oxygen as described previously[6] while rates of chain initiation (R_i) were determined for each run by the induction period method using 2,6-di-*tert*-butyl-4-methoxyphenol as the inhibitor.[7] Oxidizabilities, $k_p/(2k_t)^{1/2}$, were calculated from the kinetic expression

$$\frac{-d[O_2]}{dt} = \frac{k_p[RH]R_i^{1/2}}{(2k_t)^{1/2}} \qquad (I)$$

where k_p and $2k_t$ are the rate controlling propagation and termination rate constants.

1-Bromo-2-methyl-2-hydroperoxypropane and 1-chloro-2-methyl-2-hydroperoxypropane were the only reaction products that could be detected.[8]

Absolute values of $2k_t$ were determined by kinetic electron spin resonance spectroscopy[10] and values of k_p were calculated from eq I.

Both **1** and **2** undergo autoxidation relatively rapidly (i.e., relative to a hydrocarbon with an unactivated tertiary hydrogen, such as 2-methylpropane). The rate of autoxidation of **1** in the absence of $(CH_3)_3COOH$ does, however, increase as the partial pressure of oxygen above the liquid is reduced. This may be because some of the β-bromoalkyl radicals formed during autoxidation undergo β-scission to give isobutylene and a bromine atom (reaction 1) rather than combine with oxygen to give a peroxy radical (reaction 2). The enhanced rate of autoxidation of **1** may, therefore, be because of the involvement of Br· in rate controlling

Table I. Kinetic Data for the Autoxidation of $(CH_3)_2CHCH_2Br$ **1** and $(CH_3)_2CHCH_2Cl$ **2** in the Absence and Presence of *tert*-Butyl Hydroperoxide at 30°

Substrate	Concen (*M*)	$[(CH_3)_3COOH]$ (*M*)	10^7R_i ($M\ sec^{-1}$)	$10^7(-d[O_2]/dt)$ ($M\ sec^{-1}$)	$10^3(k_p/(2k_t)^{1/2})$ ($M^{-1/2}\ sec^{-1/2}$)	k_p ($M^{-1}\ sec^{-1}$)	$10^{-6}(2k_t)$ ($M^{-1}\ sec^{-1}$)
1	9.2		0.2	1.5	0.12	0.07	0.36
1[a]	9.2		0.2	3.4	0.27		
1[b]	9.2		0.2	145	11		
1	8.3	0.5	1.6	16	0.48	0.017	0.0012[c]
1	7.4	2.0	1.7	16	0.52	0.018	0.0012[c]
1[a]	7.4	2.0	6.0	30	0.52	0.018	
1[b]	7.4	2.0	4.0	24	0.52		
2	9.4		0.2	~0.3[d]	~0.02[d]	~0.02[d]	1.2
2	8.5	1.0	0.2	1.25	0.11	0.004	0.0012[c]
2	7.5	2.0	0.2	0.85	0.08	0.003	0.0012[c]

[a] O_2 pressure = 140 Torr. [b] Containing 0.04 *M* HBr. [c] Calculated from the kinetic expression $\log (2k_t/M^{-1}\ sec^{-1}) = 9.2 - 8.5/\theta$, where $\theta = 2.3RT$(kcal mol^{-1}),[11] the measured rate constants in these systems agreed with this value within experimental error. [d] Approximate values because of the low kinetic chain length.

$$(CH_3)_2\dot{C}CH_2Br \longrightarrow (CH_3)_2C{=}CH_2 + Br\cdot \qquad (1)$$

$$(CH_3)_2\dot{C}CH_2Br + O_2 \longrightarrow (CH_3)_2C(OO\cdot)CH_2Br \qquad (2)$$

propagation reactions. The sensitivity of an autoxidation to Br· is illustrated by the observation that the oxidizability of **1** is increased by a factor of ~100 by the addition of 0.04 *M* HBr.

The rate of autoxidation of **1** in the presence of $(CH_3)_3COOH$ (0.5 to 2 *M*) does not depend on the partial pressure of oxygen indicating that reaction 1 is not important in this system. This is not unexpected because at such large hydroperoxide concentrations any bromine atoms that are formed should undergo chain transfer with the hydroperoxide to regenerate peroxy radicals.

$$Br\cdot + (CH_3)_3COOH \longrightarrow HBr + (CH_3)_3COO\cdot \qquad (3)$$

This was confirmed by the observation that catalysis of the oxidation of **1** by HBr was eliminated by 2 *M* $(CH_3)_3COOH$ (vide Table I).

The only rate controlling propagation reaction in this system is, therefore

$$(CH_3)_3COO\cdot + (CH_3)_2CHCH_2X \xrightarrow{k_p'} (CH_3)_3COOH + (CH_3)_2\dot{C}CH_2X \qquad (4)$$

and the propagation rate constant that is measured is k_p'.

Measurements of homopropagation rate constants at 30° for organic substrates with unactivated C–H's (e.g., isobutane **3**) and organic substrates with α-bromo and α-chloro substituents (e.g., isopropyl bromide **4** and isopropyl chloride **5**) is not possible because kinetic chain lengths are too short.[11] A propagation rate constant of 0.003 M^{-1} sec^{-1} for the autoxidation of **3** has, however, been estimated[11] while rate constants for reaction of **4** and **5** with $(CH_3)_3COO\cdot$ have been calculated to be ~0.0006 M^{-1} sec^{-1}.[11]

The reactivity of compounds **1** to **5** to $(CH_3)_3COO\cdot$ decreases in the order **1** > **2** ~ **3** > **4** ~ **5** whereas on purely electronic grounds the reactivity order should be **3** > **1** ~ **2** > **4** ~ **5**. Thus a CH_2Br group activates an adjacent C–H bond relative to a CH_3 group because anchimeric assistance from the β-bromine overshadows the deactivating effect expected from electron withdrawal by the bromine. The similarity between the rate constants for **3** and **2** implies that the deactivating effect of a β-chloro substituent is almost exactly balanced by the accelerating effect from anchimeric assistance.

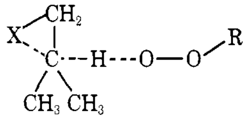
We have previously concluded[11] that rate constants for reaction of organic compounds with $(CH_3)_3COO\cdot$ at 30° correlate with the strength of the weakest bond in the molecule (D[R–H]) by the empirical equation

$$\log (k_p'/M^{-1}\ \mathrm{sec}^{-1}) = 15.4 - 0.2D[\mathrm{R{-}H}]$$

with D[R–H] in kilocalories per mole. As values of k_p' for **1** and **2** would be expected to fit this relationship **1** must have a tertiary C–H bond that is ~7 kcal mol^{-1} weaker than **4** and ~4 kcal mol^{-1} weaker than **3**, while the tertiary C–H's in **2** and **3** have approximately the same strength.

The estimated stabilizing effect of a CH_2Br substituent relative to a CH_3 substituent of 4 kcal mol^{-1} is in reasonable agreement with the estimate of 2.5 kcal mol^{-1} obtained by Cain and Solly[12] from a kinetic study of the thermolysis of 1-bromomethyl- and 1-methyl-4-chlorobicyclo[2.-2.0]hexanes and the estimate of 3 kcal mol^{-1} made by Skell and Shea[13] from a study of the brominations of 1-bromobutane and propane.

We believe that the enhanced reactivity of a H atom β to a bromine and chlorine substituent to t-ROO· provides unequivocal support for the bridged radical postulate favored by Skell and coworkers.[2] This means that the transition state for reaction 4 contains a stabilizing contribution from[14]



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J. H. Bernard Chenier, J. Paul-Alain Tremblay[16]
James A. Howard*

Division of Chemistry, National Research Council
Ottawa, Ontario, Canada

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Regiospecific Synthesis of Trimethylsilyl Enol Ethers via Silatropic Rearrangements

Sir:

Trimethylsilyl enol ethers are proving to be versatile intermediates in organic synthesis. In addition to serving as convenient precursors for the formation and alkylation of specific enolate anions,[1] trimethylsilyl enol ethers undergo oxidative functionalization reactions with strong electrophiles to give heterosubstituted carbonyl compounds,[2] oxidative cleavage with ozone,[3a] Schmidt-type rearrangement with sulfonyl azides,[3b] cyclopropanation with iodomethyl zinc iodide,[3c] titanium tetrachloride catalyzed aldol condensation with acetals, aldehydes, and ketones,[4] and acylation with acid chlorides[2a] and isocyanates.[5] The principal method for the preparation of trimethylsilyl enol ethers has been silylation of enolate anions, the scope of which is defined by the procedures for the regiospecific generation of enolate anions.[6] We wish to report that thermal silatropic rearrangements,[7] formally analogous to known prototropic pro-