

Figure 6. Correlation of free energies of activation for heterolysis of the nitroxyls from 5-H-6-MeU* with those (ref 9) from CH₃ĊHOH.

of heterolysis reaction, results as 1.0, in agreement with the individually determined ρ values (both 1.5). This is additional evidence for the close resemblance of the CH₃ĊHOH and 5-H-6-MeU* systems. In contrast, when ΔG^\ddagger values for the heterolysis of the nitroxyls from 5-OH-6-MeU* or 5-OH-6-Me-*i*-C* are plotted versus those for the nitroxyls from CH₃ĊHOH, the correlation coefficients are only 0.93 and 0.92, respectively, which indicates that CH₃ĊHOH is not a good model for the 5-hydroxy-6-yl radicals. That these belong to a class of their own is shown not only by their similar solvent kinetic isotope effect (1.2-1.4) but also by the good correlation ($r = 0.98$) between their corresponding ΔG^\ddagger values.

As seen in Table IV, reactions of 5-hydroxy-6-methyl-6-yl radicals from two additional pyrimidines were studied. As compared to that from 6-methyluracil, the radical from 1,3,6-trimethyluracil shows a higher reactivity with both 4-NAP and 4-NBN, as judged by both k_t and k_{hs} . This demonstrates the increase in electron density resulting from the additional methyl groups at N-1 and N-3. Of particular interest are the strongly negative activation entropies. Since there is no proton at N-1 whose transfer, in the transition state, to adjacent water molecules can lead to their freezing,³⁸ the negative values probably originate from immobilization of H₂O molecules caused by the ions pro-

(38) Hydration of a proton by four water molecules leads to an entropy loss of 105 J mol⁻¹ K⁻¹ (cf. Frost, A. A.; Pearson, R. G. *Kinetics and Mechanism*, Wiley: New York, 1961; Buschmann, H.-J.; Dutkiewicz, E.; Knoche, W. *Ber. Bunsen-Ges. Phys. Chem.* 1982, 86, 129.

duced on hydration of the (incipient) C-6 carbocation. An analogous effect has been observed³⁹ in the case of trialkoxymethyl carbocations.

The radical from 2-amino-4,6-dimethylpyrimidine appears to react with nitrobenzenes by electron transfer: no evidence for nitroxyl-type adducts was found.

Summary and Conclusions

It has been shown that the OH or H adducts to the 5-position of 6-methyluracil and of 6-methylisocytosine react with nitrobenzenes to give partly electron-transfer products (radical anions) and partly nitroxyl radicals (via addition). The nitroxyl radicals undergo a unimolecular heterolysis reaction that gives additional radical anion. The heterolysis, which is analogous to solvolysis of nonradical tetrahedral intermediates,⁴⁰ is essentially entropy controlled. The addition/elimination sequence⁴¹ is an example for inner-sphere⁴² electron transfer.

The rate constants k_t for reaction of the pyrimidin-6-yl radicals and the rate constants k_{hs} and the activation parameters for the heterolysis can be used to scale the reducing properties of these radicals. On this basis, the 5-hydroxy-6-methyl-6-yl radicals (i.e., the OH adducts) are considerably weaker reductants than the corresponding 5-hydroxyl radicals (i.e., the H adducts¹⁹), in agreement with earlier results.¹² The cytosin-6-yl is a more potent electron donor than that from uracil. As compared to simple aliphatic radicals with known redox potential,³⁴ 5-H-6-MeU* is very similar to CH₃ĊHOH, 5-OH-6-MeU* is comparable to HOCH₂ĊHOH, and the OH adduct to uracil itself, 5-hydroxyuracil-6-yl,¹² resembles ĊH₂OH.

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(39) Steenken, S.; Buschek, J.; McClelland, R. A. *J. Am. Chem. Soc.* 1986, 108, 2808.

(40) For reviews on tetrahedral intermediates see, e.g., (a) Cordes, E. H. *Prog. Phys. Org. Chem.* 1967, 4, 1. (b) Fife, T. H. *Acc. Chem. Res.* 1972, 5, 264. (c) McClelland, R. A.; Santry, L. J. *Acc. Chem. Res.* 1983, 16, 394. (d) Capon, B.; Dosunmu, M. I.; Sanchez, M. N. M. *Adv. Phys. Org. Chem.* 1985, 21, 37.

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(42) cf. Ebersson, L. *Adv. Phys. Org. Chem.* 1982, 18, 79.

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Rate Constants for Oxidation Reactions by Radical Cations from Methyl Iodide

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Radical cations from methyl iodide, CH₃I^{•+}, and (CH₃I[•]:ICH₃)⁺ are shown to be excellent oxidants with a one-electron redox potential presumably $\geq +2$ V. Absolute rate constants in the order of 10⁹ M⁻¹ s⁻¹ have been determined for their reactions with various organic sulfides, disulfides, thiols, phenothiazines, and inorganic metal and halide ions. A similarly high reactivity has also been found for the hydroxyl radical adduct to methyl iodide, CH₃I(OH)^{•+}. The results are discussed in view of the electronic and steric structure of these oxidizing radical species and the substrates to be oxidized.

Introduction

One-electron oxidation of alkyl iodides leads to two different kinds of radical cations.¹ They have been suggested to be con-

nected in the equilibrium



i.e., their actual yield is a function of the RI concentration and the equilibrium constant. For the methylated species (R = CH₃)

(1) Mohan, H.; Asmus, K.-D. *J. Chem. Soc., Perkin Trans. 2*, in press.

the latter has been estimated to $K \geq 5 \times 10^4 \text{ M}^{-1}$ in aqueous solution.¹ The electronic structure of the dimer complex $(\text{RI}:\text{IR})^+$ is characterized by a $2\sigma/1\sigma^*$ three-electron bond which contains two bonding and one antibonding electron between the two iodine atoms.¹ While the identity of this species appears to be independent of the solvent or matrix,¹⁻³ this is probably not true for the radical cation denoted as $\text{RI}^{+\bullet}$. In aqueous solution, for example, the latter is most likely associated with one water molecule and should more precisely be referred to as $(\text{RI}:\text{OH}_2)^+$.¹

Its deprotonated form is also well-known, namely, as the $\bullet\text{OH}$ adduct to the alkyl iodide.^{4,5} Generally, this is written as $\text{RI}(\text{OH})\bullet$ but in analogy may be expressed as $\text{RI}:\text{OH}$. The neutral $\bullet\text{OH}$ adduct and the monoalkyl iodide radical cation appear indeed to be linked via an acid base equilibrium with a $\text{p}K \sim 3.5$.¹ Accordingly, the radical cations are only formed at low pH in aqueous solution. It is noted that analogous species to $(\text{RI}:\text{OH}_2)^+$ and $\text{RI}:\text{OH}$ have been found and described in the oxidation of organic sulfides.⁶⁻⁸

For convenience and easy distinction we will use the three-electron bond notation generally only for the $(\text{RI}:\text{IR})^+$ complex. The other two species will mainly be referred to as $\text{RI}^{+\bullet}$ and $\text{RI}(\text{OH})\bullet$ in the following.

Identification of all these radicals in solution has been achieved by the radiation chemical technique of pulse radiolysis. Time-resolved optical and conductivity measurements have, for example, revealed half-lives in the order of 10–30 μs for all three types of species.¹ Such lifetimes are long enough to study the reactivities of these species toward additives. In a recent publication we have reported that $(\text{CH}_3\text{I}:\text{ICH}_3)^+$ radical cations are able to oxidize I^- and $(\text{CH}_3)_2\text{S}$ with high rate constants of $>10^9 \text{ M}^{-1} \text{ s}^{-1}$.¹ This suggests that oxidized alkyl iodides may generally be powerful oxidants. In the present paper we now confirm this early conclusion by reporting on the kinetics for a large number of oxidation reactions which are initiated by $\text{CH}_3(\text{OH})\bullet$, $\text{CH}_3\text{I}^{+\bullet}$, and $(\text{CH}_3\text{I}:\text{ICH}_3)^+$.

Experimental Section

The aqueous solutions were prepared from deionized, "Millipore" filtered water. Most solutes were obtained commercially at their highest possible purity. If necessary, further purification was achieved via standard methods (recrystallization, distillation, etc.). Methyl iodide was always freshly distilled for each set of experiments. 6-endo-(Methylthio)bicyclo[2.2.1]heptane-2-endo-carboxylic acid⁹ and 1-iodo-3-methylthiopropane¹⁰ were synthesized and purified according to the literature.

Deoxygenation of the water was achieved by bubbling it with N_2 (ca. 1 h/dm³). Subsequently the water was saturated with N_2O . This solute converts hydrated electrons—which are formed at about equal yield as hydroxyl radicals upon radiolysis of aqueous systems—into hydroxyl radicals via $\text{N}_2\text{O} + e_{\text{aq}}^- \rightarrow \text{N}_2 + \text{OH}^- + \bullet\text{OH}$. After this treatment with $\text{N}_2/\text{N}_2\text{O}$ the other solutes are generally added through gas-tight septa and dissolved by magnetic stirring.

Irradiations were carried out by means of pulse radiolysis. The characteristic features of this radiation chemical technique including the analysis of data have been described elsewhere.¹¹ The radical species were generated by short pulses of high-energy (1.5 MeV) electrons from a van de Graaff accelerator. Pulse lengths

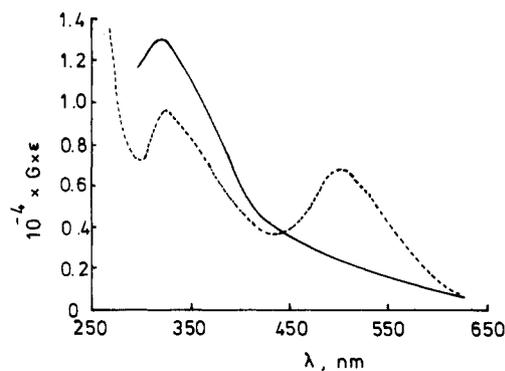


Figure 1. Solid curve: optical absorption spectrum of $\text{CH}_3\text{I}^{+\bullet}$, obtained immediately after a 1- μs pulse in an N_2O saturated, pH 3.1 aqueous solution of 10^{-4} M CH_3I . Dashed curve: optical absorption spectrum, obtained 10 μs after the pulse in the above solution which contained also $2 \times 10^{-5} \text{ M}$ promethazine (PZH^+).

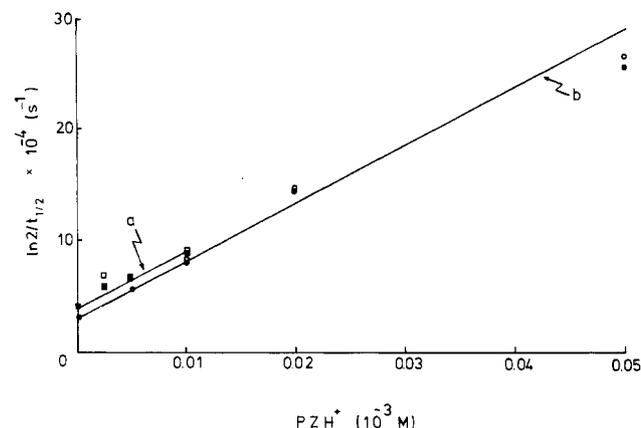


Figure 2. First-order rate constants $k = \ln 2/t_{1/2}$ for the oxidation of promethazine as a function of PZH^+ concentration, obtained from pulse radiolysis of N_2O saturated, pH 3.5 aqueous solutions of 10^{-4} M (a) and $8 \times 10^{-3} \text{ M}$ (b) CH_3I : (O, \square) formation at 510 nm; (\bullet , \blacksquare) decay at 410 nm.

were typically in the order of 1 μs , and absorbed doses per pulse amounted to 1–2 Gy ($\text{J}\cdot\text{kg}^{-1}$). In N_2O -saturated solutions ca. 90% of the primary species is $\bullet\text{OH}$ radicals. Their radiation chemical yield amounts to $G \approx 6$ species per 100 eV of absorbed energy or in terms of concentration to about $10^{-6} \text{ M}/1\text{-}2\text{-Gy}$ pulse.

Experimental error limits were minimized by signal averaging and generally did not exceed $\pm 5\%$ for an individual experiment. Error limits for the rate constants are given in the tables. All experiments were carried out at room temperature.

Results

1. Oxidations by $\text{CH}_3\text{I}^{+\bullet}$ and $(\text{CH}_3\text{I}:\text{ICH}_3)^+$ Radical Cations. The molecular radical cation $\text{CH}_3\text{I}^{+\bullet}$ (or $(\text{CH}_3\text{I}:\text{OH}_2)^+$, see Introduction and Discussion) is generated in the $\bullet\text{OH}$ -induced oxidation of CH_3I at low pH and low solute concentration.¹ Its absorption spectrum obtained upon pulse radiolysis of an N_2O -saturated, pH 3.1 solution of 10^{-4} M methyl iodide is exhibited in Figure 1 (solid curve). The characteristic feature is a maximum at 310 nm. The slight shoulder at $>400 \text{ nm}$ is due to $(\text{CH}_3\text{I}:\text{ICH}_3)^+$ formed to a small extent via the equilibrium



at this solute concentration. The $\text{CH}_3\text{I}^{+\bullet}$ absorption, under these conditions, decays with a half-life of 20 μs .

Addition of small amounts of oxidizable substrates generally leads to an accelerated, exponential decay of the $\text{CH}_3\text{I}^{+\bullet}$ absorption with half-lives which decrease with increasing substrate concentration. An example is the oxidation of promethazine, PZH^+ ,



which results in the formation of the promethazine radical cation. The absorption of the latter is contained in the dashed curve in

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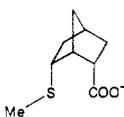
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TABLE I: Rate Constants for the Oxidation of Various Compounds by $\text{CH}_3\text{I}^{+\bullet}$ and $(\text{CH}_3\text{I}\cdot\text{ICH}_3)^{+\bullet}$

substrate S	$[\text{CH}_3\text{I}]$, M	$k[\text{CH}_3\text{I}^{+\bullet}/(\text{CH}_3\text{I}\cdot\text{ICH}_3)^{+\bullet} + \text{S}]$, $10^9 \text{ M}^{-1} \text{ s}^{-1}$	oxidized substrate identified by optical absorption	ref
Me_2S	1×10^{-3}	3.6 ± 0.5	$(\text{Me}_2\text{S}\cdot\text{SMe}_2)^{+\bullet}$	28
	3×10^{-3}	3.1 ± 0.5	$(\text{Me}_2\text{S}\cdot\text{SMe}_2)^{+\bullet}$	
	5×10^{-3}	4.0 ± 0.5	$(\text{Me}_2\text{S}\cdot\text{SMe}_2)^{+\bullet}$	
Et_2S	3×10^{-3}	2.9 ± 0.7	$(\text{Et}_2\text{S}\cdot\text{SEt}_2)^{+\bullet}$	28
	3×10^{-3}	2.0 ± 0.7		
<i>i</i> -Pr ₂ S	3×10^{-3}	1.9 ± 0.7		
<i>n</i> -Bu ₂ S	3×10^{-3}	1.5 ± 0.8		
<i>s</i> -Bu ₂ S	3×10^{-3}	1.7 ± 0.8		
<i>t</i> -Bu ₂ S	3×10^{-3}	3.0 ± 0.5	$(\text{PhSMe})^{+\bullet}$	29
PhSMe	3×10^{-3}	2.0 ± 1.0		
methionine	3×10^{-3}	3.0 ± 0.6	$(\text{Me}_2\text{S}_2)^{+\bullet}$	30
Me_2S_2	3×10^{-3}	1.9 ± 0.7	$(\text{Et}_2\text{S}_2)^{+\bullet}$	30
Et_2S_2	3×10^{-3}	1.0 ± 0.7		
<i>n</i> -Pr ₂ S ₂	3×10^{-3}	1.5 ± 0.5		
<i>i</i> -Pr ₂ S ₂	3×10^{-3}	0.8 ± 0.4		
<i>n</i> -Bu ₂ S ₂	3×10^{-3}	0.9 ± 0.5		
<i>s</i> -Bu ₂ S ₂	3×10^{-3}	0.4 ± 0.3	$(\text{t-Bu}_2\text{S}_2)^{+\bullet}$	30
<i>t</i> -Bu ₂ S ₂	3×10^{-3}	3.0 ± 1.0	$\text{lip}(\text{S}_2)^{+\bullet}$	21
lipoic acid	3×10^{-3}	4.2 ± 0.8		
EtSH	3×10^{-3}	2.9 ± 0.6		
<i>n</i> -PrSH	3×10^{-3}	3.4 ± 0.6		
<i>i</i> -PrSH	3×10^{-3}	3.0 ± 0.6		
<i>t</i> -BuSH	3×10^{-3}	3.6 ± 0.6	PhS [•]	25
PhSH	3×10^{-3}	3.2 ± 0.5		
cysteine	3×10^{-3}	4.2 ± 0.6	PZH ²⁺	12
promethazine	1×10^{-4}	4.8 ± 0.6		
	1×10^{-3}	4.8 ± 0.6		
	3×10^{-3}	4.8 ± 0.6		
	8×10^{-3}	4.5 ± 0.6		
	1.2×10^{-2}	5.2 ± 0.6		
chlorpromazine	3×10^{-3}	4.2 ± 0.8	CPZ ²⁺	12
$\text{MeS}(\text{CH}_2)_3\text{I}$	2×10^{-4}	2.9 ± 1.0		31
<i>t</i> -BuS(CH ₂) ₃ I	2×10^{-4}	1.5 ± 1.0		
	2×10^{-4}	2.0 ± 1.0		32
Ti^{2+}	2×10^{-4}	(2.5)	Ti^{2+}	33
Ag^+	3×10^{-3}	1.0 ± 0.5	Ag^{2+}	34
I^-	3×10^{-3}	7.7 ± 1.0	$\text{I}_2^{\bullet-}$	35
Br^-	3×10^{-3}	4.0 ± 2.0	$\text{Br}_2^{\bullet-}$	35
Cl^-	3×10^{-3}	5.0 ± 2.0	$\text{Cl}_2^{\bullet-}$ (?)	35
SCN^-	3×10^{-3}	5.0 ± 2.0	$(\text{SCN})_2^{\bullet-}$	35

^aSolutions: N₂O saturated, pH 3.0–3.5, 2×10^{-6} to 10^{-4} M of oxidizable compounds. (ref refers to absorption of oxidized substrates.)

Figure 1.¹² The first-order rate constants $k = \ln 2/t_{1/2}$ as derived from the $\text{CH}_3\text{I}^{+\bullet}$ decay at 310 nm or the PZH²⁺ formation at 505 nm are plotted vs the PZH²⁺ concentration in Figure 2a. A straight line is obtained with an intercept at $k = 3.9 \times 10^4 \text{ s}^{-1}$, which corresponds to the $\text{CH}_3\text{I}^{+\bullet}$ decay in the absence of PZH²⁺. The bimolecular rate constant for reaction 3 is given by the slope and amounts to $k_3 = 4.2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$.

The same rate constant (within the $\pm 10\%$ experimental limit of error) is obtained for solutions which contained different concentrations of methyl iodide (10^{-3} , 3×10^{-3} , 8×10^{-3} , and 12×10^{-3} M). In these solutions the equilibrium reaction 2 is increasingly shifted toward the three-electron-bonded dimer radical cation. The kinetic data for the 8×10^{-3} M CH_3I solution, for example, are displayed in Figure 2b. For all high concentration solutions the respective first-order rate constants were derived from the decay of the $(\text{CH}_3\text{I}\cdot\text{ICH}_3)^{+\bullet}$ absorption at 415 nm. The slope of the straight line in Figure 2b is practically the same as in Figure 2a. The intercept differs slightly and now corresponds to the decay of the three-electron-bonded species in the absence of promethazine ($k = 3.1 \times 10^4 \text{ s}^{-1}$).

The fact that practically identical rate constants are obtained with solutions of different methyl iodide concentration indicates

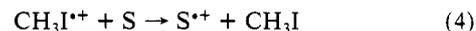
TABLE II: Rate Constants for the Oxidation of Various Compounds by $\text{CH}_3\text{I}(\text{OH})^{\bullet}$

substrate S	$k[\text{CH}_3\text{I}(\text{OH})^{\bullet} + \text{S}]$, $10^9 \text{ M}^{-1} \text{ s}^{-1}$	oxidized substrate identified by optical absorption	ref
Me_2S	1.5 ± 1.0	$(\text{Me}_2\text{S}\cdot\text{SMe}_2)^{+\bullet}$	28
Et_2S	1.5 ± 1.0	$(\text{Et}_2\text{S}\cdot\text{SEt}_2)^{+\bullet}$	28
<i>t</i> -Bu ₂ S	1.5 ± 1.0		
methionine	1.4 ± 1.0		
Me_2S_2	1.3 ± 1.0	$(\text{Me}_2\text{S}_2)^{+\bullet}$	30
<i>t</i> -Bu ₂ S ₂	1.5 ± 1.0	$(\text{t-Bu}_2\text{S}_2)^{+\bullet}$	30
lipoic acid	1.3 ± 1.0	$\text{lip}(\text{S}_2)^{+\bullet}$	21
EtSH	2.8 ± 1.0		
<i>t</i> -BuSH	2.0 ± 1.0		
PhSH	2.0 ± 1.0	PhS [•]	25
cysteine	2.5 ± 1.0		
promethazine	2.3 ± 1.0	PZH ²⁺	12
chlorpromazine	2.2 ± 1.0	CPZ ²⁺	12
I^-	2.0 ± 1.0	$\text{I}_2^{\bullet-}$	35
SCN^-	2.2 ± 1.0	$(\text{SCN})_2^{\bullet-}$	35

^aSolutions: N₂O saturated, pH 7–10, 3×10^{-3} M CH_3I , 2×10^{-6} to 10^{-4} M of oxidizable compounds. (ref refers to absorption of oxidized substrate.)

that both radical cations, $\text{CH}_3\text{I}^{+\bullet}$ and $(\text{CH}_3\text{I}\cdot\text{ICH}_3)^{+\bullet}$, are equally good oxidants.

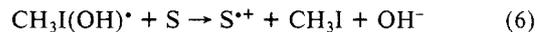
Qualitatively similar results have been obtained for many other oxidizable compounds. The rate constants were derived from the decay of the $\text{CH}_3\text{I}^{+\bullet}$ (310 nm) or $(\text{CH}_3\text{I}\cdot\text{ICH}_3)^{+\bullet}$ (415 nm) absorption and/or the formation kinetics of the oxidized additive whenever possible. The results which refer to the general reactions



are listed in Table I ($\text{S}^{+\bullet}$ denotes the one-electron oxidation form of the substrate S irrespective of its actual charge and hydrolysis status). The table also includes the transients which could directly be identified as the result of the oxidation processes.

2. Oxidations by $\text{CH}_3\text{I}(\text{OH})^{\bullet}$. Under less acidic conditions (pH > 5) the $\cdot\text{OH}$ -induced oxidation of alkyl iodides leads to the neutral adduct radical, namely, $\text{CH}_3\text{I}(\text{OH})^{\bullet}$.^{1,4,5} This has an optical absorption with two bands at 310 and 350 nm which may be used for kinetic measurements.

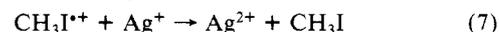
A selected but nevertheless representative group of substrates was investigated with respect to an oxidation by this neutral radical. Generally these experiments were carried out with N₂O-saturated solutions of 3×10^{-3} M CH_3I and comparatively smaller substrate concentrations ($\leq 10^{-4}$ M) at pH 7 and 10. The bimolecular rate constants for the general reaction



(Table II) are slightly lower but nevertheless of the same order of magnitude as for the radical cation induced oxidations.

Discussion

The results identify $\text{CH}_3\text{I}^{+\bullet}$, $(\text{CH}_3\text{I}\cdot\text{ICH}_3)^{+\bullet}$, and $\text{CH}_3\text{I}(\text{OH})^{\bullet}$ as excellent oxidants, and it is probably valid to generalize this statement for the corresponding radical species from other alkyl iodides. It is particularly noted that even metal and halide ions are oxidized at practically diffusion-controlled rates. In case of silver ions, for example, the reaction



leads to Ag^{2+} ions, which are excellent oxidants themselves.^{13–15} In fact, we could not detect any signs for a reversibility of reaction 7, i.e., an oxidation of CH_3I by Ag^{2+} . This means that the $\text{CH}_3\text{I}^{+\bullet}/\text{CH}_3\text{I}$ oxidation potential must be appreciably more positive than $E^0 = +1.98$ V for the $\text{Ag}^{2+}/\text{Ag}^+$ couple.¹⁵

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The result on the oxidation of TI⁺ is not free of ambiguity. A linearity between $\ln 2/t_{1/2}$ and TI⁺ concentration was only observed at [TI⁺] ≤ 10⁻⁵ M for reasons which could not yet be evaluated.

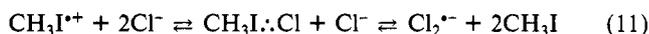
Caution should also be applied in case of the oxidation of chloride ions. The radical cations and the CH₃I(OH)[•] clearly react with Cl⁻, and the product radical absorption with $\lambda_{\max} = 350$ nm is compatible with that of Cl₂^{•-}. An assignment of the underlying process to



(or a corresponding oxidation by (CH₃I₂:ICH₃)⁺) would thus be reasonable. But there is an alternative possibility which should be considered, namely, the formation of a neutral CH₃I₂:Cl, e.g., via addition of a chloride ion to the radical cation

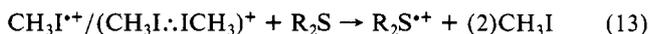


Furthermore, this adduct may be involved in an equilibrium system



although we could not detect any indication for an oxidation of CH₃I by Cl₂^{•-}. The rationale behind this consideration is an analogous observation in the oxidation of organic sulfides where R₂S₂:Cl has been identified in the reaction of R₂S^{•+} with Cl⁻.¹⁶ Also by extrapolation from the sulfide system, any CH₃I₂:Cl may have an absorption not too different from that of Cl₂^{•-}. Finally, a CH₃I₂:Cl would constitute a species similar to RI₂[•] (RI₂:I), which has been claimed as a transient in irradiated solid alkyl iodide matrix^{2,3} and also some liquid solutions.^{4,17} Therefore, an unambiguous assignment is not possible. If, however, the absorption was indeed due to Cl₂^{•-} and its formation was based on a straightforward one-electron transfer (reaction 8), the redox potential of the CH₃I^{•+}/CH₃I couple would even exceed +2.3 V, i.e., that of the Cl₂^{•-}/2Cl⁻ couple.¹⁸

Remarkable trends are observed for the oxidations of disulfides and sulfides



within the series of aliphatic substituents R. For these two groups of substrates the rate constants decrease slightly but steadily from R = CH₃ to R = *t*-C₄H₉ or *s*-C₄H₉. (For thiols, which are the easiest to oxidize among the sulfur compounds, a marginal effect is indicated.)

Generally an oxidation, i.e., a removal of an electron, should become increasingly favorable with increasing electron density at the oxidation site. If this was the rate-determining parameter in our case, the rate constants should follow a trend just opposite to the observed one. A more reasonable basis could be the variation of the diffusion coefficients with the size of the substrate molecules. However, this argument is also not fully satisfactory since it would not explain the relatively high rate constants observed for the oxidation of such large molecules as methionine, thioanisole, the two phenothiazines, and lipoic acid, for example.

It seems that the rate constants also reflect the steric situation at the reaction site. This is probably best illustrated by the results on the oxidation of some disulfides. Lipoic acid, dimethyl disulfide, and di-*tert*-butyl disulfide, for example, are oxidized with rate constants of 3.0 × 10⁹, 3.0 × 10⁹, and 0.5 × 10⁹ M⁻¹ s⁻¹, respectively. The first gas-phase ionization potentials of 8.06, 8.97, and 8.17 eV, respectively,¹⁹ certainly do not follow this trend, and

the same holds for the diffusion coefficients. A correlation exists, however, for the torsional CS-SC angle, which increases from 35° to 84.7° to 110° for these three disulfides, respectively.¹⁹ Lipoic acid thus provides a conformation which allows an almost unhindered approach of the oxidizing radical from the steric point of view. Furthermore, the geometrically supported possibility for sulfur-sulfur p-orbital overlap associated with the generation of doubly occupied π- and π*-orbitals would make lipoic acid more susceptible for an oxidation process (effectively this leads to a higher electron density in the disulfide bridge). In this respect it is reminded that the electronic structure of a disulfide radical cation is characterized by a sulfur-sulfur bond which contains two bonding σ-electrons, two bonding π-electrons, and one antibonding π*-electron.^{19,20} A lower oxidation rate constant would thus become understandable if the (sterically based) electronic structure of the unoxidized disulfide differs significantly from that of the (RSSR)^{•+} radical cation.²¹ Bulky substituents will, of course, also prevent an unhindered approach of the oxidant to the disulfide bridge.

Steric reasons are also put forward to account for the trend in rate constants for the oxidation of the aliphatic sulfides. In analogy to several examples with these compounds,^{8,16} it can be assumed that their oxidation by the alkyl iodide radical species proceeds via an adduct, e.g.



It is easy to realize that such close encounters become less favorable if both substituents at sulfur are bulky.

The steric factor should become less important with an increasing difference in the redox potential of the acceptor-donor pairs, which would facilitate long-range electron transfer. The fast oxidations of the phenothiazines ($E^0 \approx 0.6-0.8$ V)^{22,23} and the thiols ($E^0 \approx 0.8-1.0$ V),²⁴ in particular, may thus be explained.

Another interesting aspect in our investigation is that all three types of alkyl iodide radical species, i.e., CH₃I^{•+}, (CH₃I₂:ICH₃)⁺, and CH₃I(OH)[•], exhibit practically the same oxidative power. This is significantly different from the corresponding species derived from sulfides, where R₂S^{•+} is a much better oxidant than (R₂S₂:SR₂)⁺.^{13,25} (For R₂S(OH)[•] so far no direct oxidation reaction has been observed, which is presumably due to its extremely short lifetime.)

When the three-electron-bonded radical cations derived from tri-, di-, and monovalent hetero atoms, e.g., (R₃N₂:NR₃)⁺, (R₂S₂:SR₂)⁺, and (RI₂:IR)⁺, are compared, it is noted that their oxidative power significantly increases in this series. Thus the nitrogen-centered species exhibit only very low oxidation potentials near 0 V.²⁶ The sulfur-centered analogues are already much more eager to take up an electron and readily seem to oxidize any compound with an oxidation potential up to 1.3-1.5 V.^{13,21}

It has been mentioned already that in aqueous systems the molecular species exist most likely as associates with one water molecule, i.e., (RI₂:OH₂)⁺, (R₂S₂:OH₂)⁺, and (R₃N₂:OH₂)⁺. The bond energy between the hetero atom and oxygen is probably very low, however (estimated to ca. 20 kJ for the sulfide species²⁷).

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The $\cdot\text{OH}$ adducts essentially constitute the deprotonated form of these water associates. Owing to the difference in the electronegativities between oxygen and the heteroatoms, the three-electron bond is, of course, expected to be polarized with the more positive center at I, S, or N. In case of the $\cdot\text{OH}$ adducts to the alkyl iodides, in fact, charge-transfer complexes ($\text{RI}^{\cdot+}\cdots\text{OH}^-$) seem to exist.⁵ They exhibit not only optical absorptions with a band typical for the $\text{RI}^{\cdot+}$ component¹ but according to our present results also, and not surprisingly, practically the same chemical characteristics as $(\text{RI}\cdots\text{OH}_2)^+$. The slightly reduced oxidative power as compared to the radical cations is in full accord with the general observation that the oxidation potential of radicals decreases with decreasing protonation state.

Conclusion

The radical cations derived from methyl iodide—and probably by valid extrapolation from any alkyl iodide, i.e., $\text{RI}^{\cdot+}$ and $(\text{RI}\cdots\text{IR})^+$ —have been found to be most powerful oxidants, with a one-electron oxidation potential $\geq +2$ V (vs NHE) in aqueous

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solution. This statement seems also applicable to the neutral hydroxyl radical adducts, $\text{RI}(\text{OH})^\cdot$. All these oxidizing species can conveniently be generated in aqueous solution (depending on pH) via reaction of the alkyl iodide with hydroxyl radicals. They all seem to act exclusively as one-electron oxidants, i.e., similar to, but much more efficient than, $\text{CCl}_3\text{OO}^\cdot$, Ag^{2+} , Ti^{2+} , $\text{Br}_2^{\cdot-}$, and others commonly used in radiation chemical radical studies. The oxidized alkyl iodide radicals, in particular, appear to be much more selective oxidants than the free hydroxyl radical itself, which has a comparatively higher oxidation potential but acts predominantly via addition and abstraction reactions.

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Registry No. Me_2S , 75-18-3; Et_2S , 352-93-2; *t*- Bu_2S , 107-47-1; *n*- Bu_2S , 544-40-1; *s*- Bu_2S , 626-26-6; *i*- Pr_2S , 625-80-9; Me_2S_2 , 624-92-0; Et_2S_2 , 110-81-6; *n*- Pr_2S_2 , 629-19-6; *i*- Pr_2S_2 , 4253-89-8; *n*- Bu_2S_2 , 629-45-8; *s*- Bu_2S_2 , 5943-30-6; *t*- Bu_2S_2 , 110-06-5; EtSH , 75-08-1; *n*- PrSH , 79869-58-2; *i*- PrSH , 75-33-2; *t*- BuSH , 75-66-1; PhSH , 108-98-5; PhSMe , 100-68-5; I^- , 20461-54-5; Br^- , 24959-67-9; Cl^- , 16887-00-6; Ti^+ , 21474-65-7; Ag^+ , 14701-21-4; SCN^- , 302-04-5; $\text{MeS}(\text{CH}_2)_3\text{I}$, 93530-08-6; *t*- $\text{BuS}(\text{CH}_2)_3\text{I}$, 111349-70-3; $\text{CH}_3\text{I}^{\cdot+}$, 12538-72-6; $(\text{CH}_3)_3\text{C}\cdot$, 58180-38-4; $\text{CH}_3\text{I}(\text{OH})^\cdot$, 111378-84-8; methionine, 63-68-3; L-cysteine, 56-89-3; lipoic acid, 62-46-4; promethazine, 60-87-7; chlorpromazine, 50-53-3; 6-*endo*-(methylthio)bicyclo[2.2.1]heptane-2-*endo*-carboxylate ion, 91631-94-6.

Generalized Selection Rules for Reaction Mechanisms: Electronic Control and the Woodward–Hoffmann Rules

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A generalized selection rule (GSR) approach to the determination of symmetry-allowed pathways for reaction mechanisms is presented in which the classical selection rule (CSR) stage (defining the allowed nuclear structural changes) is augmented with a quantum or state selection rule (SSR) stage (defining the allowed electronic state changes). The CSR is shown to lead to both symmetric and asymmetric pathways. The SSR are shown, in the context of an SMO (simple molecular orbital) analysis, to reduce to the conservation of orbital symmetry with respect to the symmetry operations of the reaction coordinate and to a mechanistic interpretation in terms of the continuous independent development of each electron matter wave. A definition of synchronicity and partial synchronicity is shown to be consistent with a modification of the noncrossing rule, which is crucial to a proper determination of the state correlations. The GSR results are applied to pericyclic and Diels–Alder additions, and frontier orbital theory, and confirm that the Woodward–Hoffmann rules may be rigorously applied to both the symmetric and asymmetric paths. The crucial role of the frontier orbitals for both pericyclic and Diels–Alder reactions is shown to be the result of partial synchronicity of the paths with respect to separate π -localization and σ -formation stages.

Introduction

The success of the Woodward–Hoffmann rules¹ and Fukui's frontier orbital theory² has led to a concentration of theoretical analysis of the role of symmetry in chemical reactions toward restrictions on orbital changes (see, for example, ref 3 and 4 for representative reviews and extensive bibliographies). The rules have enjoyed widespread success, particularly for polyenic pericyclic reactions, in spite of their initial formulation in terms of orbitals defined in the context of a simple molecular orbital (SMO)

analysis. However, difficulties have been reported,^{5,6} especially for Diels–Alder reactions,⁶ where the existence of an asymmetric path has been suggested as a violation of the Woodward–Hoffmann rules. It is therefore important to determine the range of validity of these rules, preferably by deriving them from a more fundamental basis in which the symmetry arguments and the aspects that depend explicitly on the particular electronic structure model are separated. Such an analysis forms the substance of this paper.

A recent formulation of selection rules for reaction mechanisms⁷⁻⁹ has shown that the symmetry constraints may be in-

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