apical ethylidyne group, $\equiv CCH_3$, is symmetrically connected to the $H_3Fe_3(CO)_9$ triangular fragment with an average C–Fe distance of 1.947 Å. The C–C bond distance in the ethylidyne group is 1.466 Å. Other bond distances and angles are normal.

The tricobalt analogue of I, $Co_3(CO)_9CCH_3$, a member of a class of compounds that have been extensively studied,[5] has a smaller $M–C_{apical}–M$ angle (81°) and a significantly shorter M–M distance (2.467 Å).[6] The mixed alkylidyne cluster analogue, $HFeCo_2(CO)_9CCH_3$, has also been prepared and characterized.[7] In addition, the ruthenium[3,8] and osmium[8,9] analogues of I have been observed. The X-ray diffraction results on the former[10] reveal the same cluster structure as that determined here for I. The role of the apical carbon[11] and the role of the bridging hydrogens in bonding[12] are two features of cluster bonding that may be fruitfully approached by a comparative study of the electronic structures of these closely related compounds. Also, because ethylidyne has been proposed as the stable species formed from C_2H_2 and C_2H_4 chemisorption on metal surfaces,[13] the properties of I are pertinent to the metal cluster–metal surface analogy[14] as applied to iron.

The aliphatic $\equiv CCH_3$ moiety results from the reduction of CO originally bound to iron. This has been demonstrated by preparing I from ^{13}C enriched $Fe(CO)_5$ (about 30%). The CO's and CH_3 group of the product I exhibited roughly equal ^{13}C enrichments as measured by ^{13}C NMR. Although the specific mechanism for the formation of I is not presently known, there is ample precedent in the literature for the type of reaction that must take place.[15] For example, the reaction of iron bound carbonyl with hydride has been shown to yield formyl complexes,[16] and the reaction of boranes with iron acetyl complexes has been shown to yield alkyliron species.[17] Particularly pertinent is the demonstrated tautomeric interconversion between methyl and hydrido methylene ligands in a triosmium carbonyl cluster and the ultimate conversion of both species to $Os_3(\mu_2\text{-}H)_3(CO)_9(\mu_3\text{-}CH)$.[18] The conversion of iron bound carbonyl to hydrocarbons by hydride has been demonstrated, e.g., $Cp_2Fe_2(CO)_4$,[19] and I, II, and III must be considered as possible intermediates in such reactions.

The isolation of compound I is of significant interest for other reasons as well. It is the first example of the formation of a member of this class of well-known trinuclear clusters from a mononuclear metal carbonyl. When the general decrease in thermal stability of hydrido derivatives in going from Os to Ru to Fe is considered,[20] the evident stability of I is further proof of the intrinsic stability of alkylidyne trinuclear metal systems.

Details of the structure and other related investigations will be presented in a subsequent publication.

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π- and σ-Acetoxy Radicals

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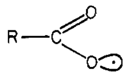
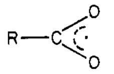
We report here the intermediacy of two types of acetoxy radicals in chain reactions, one as a hydrogen abstractor of low selectivity in alkane halogenation and the other undergoing decarboxylation (Hundsdiecker reaction) exclusively. This behavior is analogous to that shown by succinimidyl radicals,[1] and it is possible that the acetoxys may also be represented as σ and π radicals.



σ



π

All previous work on acetoxy radical recognized cage decarboxylation ($k = 1.6 \times 10^9\ s^{-1}$)[2] as the major pathway, with indications that cage-wall trapping by cyclohexene solvent is the only reaction which competes with decarboxylation; no authenticated noncage reactions were recognized.[3] We observe acetoxy reactions outside the cage which we attribute to π-acetoxy and we attribute all previous work to σ-acetoxy. Acetoxy radical is generated in chain reactions of acetyl hypobromite ($MeCO_2Br$).

Until recently acetyl hypobromite had not been available as the pure substance. We confirm its reported isolation[4] and have improved on the method by using Freon 11 in place of CCl_4, obtaining pure crystalline material in 50–60% yield.

In the absence of H donors, irradiation of solutions of acetyl hypobromite in Freon 11 at −78 °C result in quantitative conversion to methyl bromide and carbon dioxide (Hundsdiecker). These are chain reactions, both in the presence of 10^{-3} M Br_2 or

$$CH_3CO_2Br + CH_3\cdot \rightarrow CH_3CO_2\cdot + CH_3Br$$

$$CH_3CO_2\cdot \rightarrow CH_3\cdot + CO_2$$

in solutions containing 0.1 M vinylidiene chloride as Br_2 scavenger.[5]

Brominations of alkanes were observed in oxygen-free irradiated solutions of acetyl hypobromite containing 10^{-3} M Br_2. Neo-

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(5) The chain nature of the reactions was demonstrated with propionyl hypobromite whose behavior is the same as that of acetyl hypobromite. Quantum yields for disappearance of propionyl hypobromite were carried out under the conditions described for the acetyl hypobromite reactions. Oxygen-free solutions at −78 °C were irradiated at 313 nm (λ_{max} 320 nm for acetyl hyprobromite)[4] with 10^{-3} M Br_2 or with vinylidiene chloride scavenger with or without 1-bromobutane substrate. All reactions showed an induction period of ~30 min and then rapid loss of the hypobromite. Quantum yields of 25–50 were obtained if one assumes two chains were started by each quantum of light adsorbed; these are minimum values.

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Table I. Photoinitiated Halogenations of 1:1 Neopentane-Methylene Chloride Mixtures

halogenating agent	yields[a] CO_2	yields[a] neo-$C_5H_{11}X$	yields[a] $CHCl_2X$	selectivity[b]	accountability[c]
$AcOBr/Br_2$[e]	77[d]	7	14	12	98
$AcOCl/Cl_2$[e]	66	14	28	12	96
AcOBr, $Cl_2C{=}CH_2$[f]	100	0	0		100
AcOCl, $Cl_2C{=}CH_2$[f]	98	0	0		98

[a] Yields determined by GC and expressed as percentages based on starting hypohalite. [b] Selectivity calculated from the molar ratio ($CHCl_2X$/neo-$C_5H_{11}X$) times (12 neopentane hydrogens/2 CH_2Cl_2 hydrogens) to account for the statistical factor. [c] (mmol of CO_2 + mmol of halogenated product/mmol of AcOX)100. [d] Yield of methyl bromide was 75%; yield of acetic acid was 25%. [e] 10^{-3} M. [f] 0.1 M.

pentane/methylene chloride mixtures were used. Typically these reactions (tungsten lamp irradiation, 2–3 h for 100% conversion, −78 °C, CCl_3F solvent, 0.2 M AcOBr, 10^{-3} M Br_2, 1 M neo-C_5H_{12}, and 1 M CH_2Cl_2) give CO_2 (77% yield), bromination products (21%), and acetic acid (25%). This appears to be the first report of a noncage reaction of acetoxy radical. The ratio of bromodichloromethane to neopentyl bromide is 2 ± 0.3.

In the absence of acetyl hypobromite, attempts at photobromination failed under the above conditions using various concentrations of Br_2; there was no bromination.

The same reaction conditions using acetyl hypochlorite give similar results in the presence of 10^{-3} M chlorine—66% CO_2 and 40% chlorination products. The ratio of chloroform to neopentyl chloride is 2 ± 0.3. Chlorine alone under these conditions produces neopentyl chloride exclusively; the reaction of Cl· with CH_2Cl_2 is not a significant pathway in this competition.

$AcOBr/Br_2$ under the above reaction conditions brominates 1-bromobutane—68% CO_2 and 32% halogenation products, equal amounts of 1,1-dibromobutane (11%), 1,2-dibromobutane (11%), and 1,3-dibromobutane (11%) are obtained; 1,4-dibromobutane is not produced. Bromine atom chains, if they operated at these low temperatures, would produce almost exclusively 1,2-dibromobutane (by extrapolation from higher temperatures).[6a] Little discrimination between C-2 and C-3 is a characteristic of radicals such as succinimidyl,[1] Cl·,[6b] and *t*-BuO·.[6c]

It is remarkable that in the above experiments there is no halogenation of substrates if free halogen is scavenged. Experiments in which vinylidiene chloride (0.1 M) was employed as scavenger for the halogens, all other experimental details being the same, resulted in quantitative Hundsdiecker reactions, without detectable attack on neopentane, methylene chloride, or 1-bromobutane.

The possibility that chain carriers other than acetoxy are participating must be considered: Bromine atoms do not react at −78 °C. Chlorine atoms are excluded because they show a totally different selectivity. Methyl radicals are the intermediates in the Hundsdiecker, and yet there is no halogenation of substrate. This leaves acetoxy radicals as the probable intermediate, a conclusion which is supported by observing the same selectivity for both AcOBr and AcOCl.

A reasonable hypothesis is that two different types of acetoxy are produced, one, produced in the presence of halogens, which abstracts hydrogen atoms beyond the cage with low selectivity and the other, produced in halogen-scavenged systems, which undergoes decarboxylation too rapidly for noncage encounters. The latter type of behavior had been predicted for the $^2A_1$ σ state on the grounds that $^2A_1$ correlates with ground-state CO_2.[7] The acetoxy which accounts for hydrogen atom abstraction can be assigned the $^2B_2$ σ state or the $^2A_2$ π state;[7–9] neither of these correlates with ground-state CO_2, and thus it is possible for them to escape the cage and engage in relatively nondiscriminate hydrogen atom abstractions. For convenience, the notation π is given to the hydrogen atom abstracting species and σ to the other acetoxy ($^2A_1$). The σ state ($^2A_1$) would result from attack of $CH_3\cdot$ on CH_3CO_2X and the π state (hydrogen atom abstracting intermediate) from attack of halogen atom on CH_3CO_2X.

$$\sigma \qquad CH_3\cdot + CH_3CO_2X \rightarrow CH_3X + \sigma\text{-}CH_3CO_2\cdot$$

$$\sigma\text{-}CH_3CO_2\cdot \rightarrow CH_3\cdot + CO_2$$

$$\pi \qquad X\cdot + CH_3CO_2X \rightarrow X_2 + \pi\text{-}CH_3CO_2\cdot$$

$$\pi\text{-}CH_3CO_2\cdot + RH \rightarrow CH_3CO_2H + R\cdot$$

$$R\cdot + X_2 \rightarrow RX + X\cdot$$

$$\pi\text{-}CH_3CO_2\cdot \rightarrow \sigma\text{-}CH_3CO_2\cdot \text{ and/or}$$
$$R\cdot + CH_3CO_2X \rightarrow RX + \sigma\text{-}CH_3CO_2\cdot$$

The calculations concerned with carboxylate radicals lead to no single conclusion about the ordering of the states;[7–9] they have been done at too simple a level. It is hoped that suitable calculations will become available in the future. We expect that experiments which are in progress will provide an experimental basis for energy sorting the acetoxy states.

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Chiral Aggregation Phenomena. 2. Evidence for Partial "Two-Dimensional Resolution" in a Chiral Monolayer

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We wish to report the results of a novel attempt to resolve a racemic monolayer film of a chiral surfactant spread on an aqueous subphase by seeding with crystals of one of the enantiomers. Although the investigation of monolayers at the gas-liquid interface is a well-studied and currently active field,[1] there have been relatively few reports of stereochemical phenomena in films cast from chiral surfactants.[2] In the course of comparing the surface properties of racemic *N*-α-methylbenzylstearamide with those of its two pure enantiomers,[3] we noted a considerably higher surface free energy for the racemic films on aqueous sulfuric acid subphases than for comparable films of the enantiomers. This was manifested both in terms of higher surface pressures at

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[‡] These results and experimental conditions are described more fully in the doctoral thesis of Orlean Thompson, Department of Chemistry, University of Pittsburgh, 1980.

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