7). Since it has already been shown that adsorbed oxygen and hydrogen can react to produce OH which can desorb, it seems plausible that OH should be observed for this system. The fact that OH was not observed leads us to conclude that the steady-state concentration of either H(ads) or O(ads) is very low under the conditions examined. It is known that O(abs) reacts with CO to form CO₂ which subsequently desorbs.^{12,14,15} AES analysis performed by other investigators on an active catalyst surface following reaction with H_2/CO indicated the absence of oxygen.^{32,33} We have observed that the addition of O₂ to the H_2/CO stream results in an observable OH signal. Therefore it is likely that the steady-state concentration of O(ads) is very low when

only \dot{H}_2 and CO are present which results in a low steady-state concentration of OH(ads).

Conclusions

The desorption of OH has been clearly observed following either the oxidation of H_2 or the decomposition of H_2O on a polycrystalline nickel surface. The apparant activation energies for this process range from approximately 27 to 41 kcal/mol and are believed to be a measure of the Ni–OH bond strength. In the CO + H_2/Ni system no OH was observed up to a temperature of 1350 K. This is believed to be due to an extremely low concentration of adsorbed oxygen atoms and hence, adsorbed OH.

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Electron Spin Resonance Investigation of Intramolecular Hydrogen Transfer and Alkyl Attack in Ester Cation Radicals

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Reactions of the cation radicals of a number of butyl and neopentyl ester cations have been investigated by electron spin resonance spectroscopy. Radicals are formed at cryogenic temperatures by γ -irradiation of dilute CFCl₃ frozen solutions of the esters. Ester cation radicals have been shown to be especially reactive intermediates in previous work. However, in this work a number of neopentyl ester cations have been stabilized at 77 K. The major couplings in these cations arise only from three of the protons on the terminal methyl groups of the neopentyl portion of the cation. Thus the charge is predominantly located in the neopentyl group. In this work it is shown that, on annealing, the cation radicals of certain neopentyl, *tert*-butyl, and butyl esters form alkyl radical intermediates by intramolecular hydrogen transfer, presumably to the carbonyl oxygen. These ester radicals further undergo intramolecular alkyl attack on oxygen to form a rearranged radical via a heretofore unknown mechanism. Neopentyl formate cation radical undergoes a different reaction first by loss of a *tert*-butyl cation structure to form isobutene cation radical. Selective deuteration at various positions on the alkyl side groups is used to verify the assignment of hyperfine couplings to positions on the radical structures as well as to verify the rearrangement and fragmentation reactions. The reactivity of ester cation radicals is discussed and summarized.

Introduction

Ester cation radicals formed by γ -irradiation, at cryogenic temperatures, of haloalkane solutions of the parent ester have been shown to undergo a surprising diversity of chemical reactions, some even occurring at 4.2 K.¹⁻⁷ Since most organic compounds form stable cation radicals under the same conditions, it was unexpected that the ester cation radicals should be as unstable and reactive as they are. At this time, the only ester cation radical which is stable at 77 K that has been properly identified in the literature

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is that of neopentyl formate.⁶ Since the ester cation radicals are unstable, an obvious question evolves regarding what reactions they undergo.

There are two types of reactions which have been described for ester cation radicals in solid-state Freon matrices. One is intramolecular hydrogen or proton transfer, frequently from the alcohol β -carbon, to another site on the molecule.^{2,3,5-7} Ethyl formate typifies this reaction.^{6,7}

$$\begin{array}{cccc} O & CH_3 \\ H & C & H_2 \\ H & C & CH_2 \end{array} \xrightarrow{OH} \begin{array}{c} OH & CH_2 \\ H & H & H_2 \\ H & C & CH_2 \end{array}$$
(1)

Propyl acetate undergoes a similar reaction.⁶ At times, hydrogens other than those from the β -carbon reaction, as is the case for *n*-propyl formate^{3,6} in which a hydrogen on a γ -carbon reacts and isopropyl formate⁶ in which it is a hydrogen on an α -carbon. Experimental evidence regarding the actual location of the transferred hydrogen has been reported only for methyl formate.³ By analogy with this result and accepted mass spectroscopic cation radical mechanisms, we have also generally assumed that the hydrogen has been cited as a potential site for transfer.^{8,9} We refer

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to the product of this reaction as the "hydrogen-transfer radical". It is formally a cation with a putative neutral carbon radical site.

A second mode of reactivity is fragmentation via a McLafferty rearrangement or a related mechanism. Rearrangements of this type have been proposed from mass spectroscopic studies and generally are though to originate with the hydrogen-transfer radical, even though McLafferty prefers to reserve this name for a concerted mechanism.⁸ Examples of fragmentation via the McLafferty rearrangement are the reactions of isobutyl acetate cation radical⁶ and *tert*-butyl acetate radical cation (both in CFCl₃).⁴⁻⁶

$$\begin{array}{c} H \xrightarrow{H} \xrightarrow$$

For *n*-propyl acetate, fragmentation to the allyl radical occurs via an overall double hydrogen rearrangement, another mechanism proposed from mass spectroscopy.⁶

The main thrust of this report is an elaboration of a heretofore unknown reaction sequence for the hydrogen-transfer radical. In an earlier paper we described, for ethyl formate, a reaction in which the hydrogen-transfer radical reacts through intramolecular alkyl attack on oxygen. This is illustrated below by using a deuterated form of ethyl formate for clarity.⁷

$$\begin{array}{ccc} OD & CD_2 & & O^{-CD_2} CH_2 \\ H^{-C^+} O^{-CH_2} & & H^{-C^+} OD \end{array}$$
(3)

In this work we report that this intramolecular alkyl attack is quite ubiquitous and occurs for a variety of esters. This reaction is not directly observable through mass spectroscopy since the charge to mass ratio of the cation does not change, but may have profound effects on the ultimate reactivity of an ester cation radical since a chemically new species may be formed. In addition, we report additional examples of hydrogen-transfer and fragmentation reactions, as well as matrix effects on the reactions of certain ester cation radicals.

Experimental Section

Deuterated esters were synthesized from commercially available (Aldrich Chemical Co., Sigma Chemical Co.) compounds. Reduction of trimethylacetic acid with lithium aluminum deuteride followed by esterification of the resulting alcohol with the appropriate acid was used to synthesize the neopentyl- d_2 esters. Standard esterification and transesterification techniques were used to synthesize the remaining esters. Samples were purified by GLC and structures confirmed by NMR spectroscopy. Commercially available Freons (PCR Research) were used without futher purification. Samples with 1,1,2-trichloro-1,2,2-trifluoroethane as solvent were thoroughly degassed in order to prevent formation of oxygen radicals. Samples of esters (0.03-3 mol%) were irradiated in Spectrosil quartz tubes at 77 K for doses of 0.2 Mrad. The concentration of the ester in the range used had no significant effect on the spectra obtained; slight changes in coupling constants, line widths, and occasional minor formation of bimolecular reaction products in the concentrated solutions were noted. A Varian Century ESR spectrometer with dual cavity was employed. Hyperfine splittings and g values were measured vs. Fremy's salt with A = 13.09 G and g = 2.0056.

Results and Discussion

Neopentyl Esters. Neopentyl formate, neopentyl acetate, neopentyl propionate, neopentyl butyrate, and deuterated analogues of all of these compounds were investigated in this study. All of these neopentyl esters form stable cation radicals at 77 K (Tables I and III). In these cations the spin density and charge The Journal of Physical Chemistry, Vol. 89, No. 12, 1985 2639



Figure 1. (A) First-derivative ESR spectrum of a frozen solution of neopentyl acetate in CFCl₃ after γ -irradiation and measurement at 77 K, due to the cation. The two sharp lines in the center of the spectrum are background signals. (B) Spectrum after annealing to 128 K, predominantly a doublet due to II. (C) Spectrum after annealing to 141 K, due to IIIA and II. (D) Isotropic simulation of spectrum C using parameters given in Table I. The three small marks in the central portion of the spectra are the components of the standard Fremy salt, and are separated by 13.09 G with g = 2.0056. The field increases from left to right.

density are both largely located in the C–C(CH₃)₃ bond and there is hyperfine coupling to one proton on each of the three methyl groups; thus, the neopentyl ester cation radical spectrum is typically a quartet.⁶ The spectra and structure of the neopentyl ester cation radicals are quite similar to that of neopentane cation radical itself. In neopentane there is a 41-G coupling to three protons, one on each of three of the four methyl groups.¹⁰ With analogy to the structure of neopentane cation radical proposed by Iwasaki, we feel that the neopentyl ester cation radicals all have the conformation shown below, using 2,2-dimethylpropyl-1,1-d₂ formate-d as a specific example.



The coupling in the neopentyl ester cation radicals is diminished to ca. 31-34 G, due to a partial transfer of spin density to the $-CO_2$ - electronic system. We first discuss the acetate, propionate, and butyrate, which behave quite similarly; the formate is discussed later due to its somewhat different chemistry.

Neopentyl Acetate. Neopentyl acetate (A) and two deuterated analogues, 2,2-dimethylpropyl- $1,1-d_2$ acetate (B) and 2,2-dimethylpropyl- $1,1-d_2$ acetate- d_3 (C), were investigated in this work.

Upon irradiation of solutions in $CFCl_3$ at 77 K all three compounds yield ESR spectra with the familiar four-line pattern associated with a neopentyl ester cation radical (Figures 1A, 2A, and 3A). The couplings and g values of the cations are given in Table I.

Upon annealing to approximately 130 K (see Table I for precise temperatures), the spectra of both B and C irreversibly change to the spectra shown in Figures 2B and 3B. These spectra both have a centrally located triplet due to two protons with 22-G coupling; the two outer lines in the spectra are due to some cation remaining at this temperature. The central triplet, with noticeable anisotropy in the outer lines, is characteristic of a rotating $-CH_2$ radical site. Since this spectrum appears for structure C, which

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TABLE I:	Isotropic Hyperfine	Couplings an	nd g	Values for	the Neo	pentyl.	Acetates and	Pro	pionates i	n CF	iCl ₃

ester	cation (77 K)	hydrogen-transfer radical	alkyl attack radical	other radicals
neopentyl acetate	33 G (3 H) g = 2.003		141 K CH ₃ COCH ₃ [OCH ₂ Ċ(CH ₃) ₂] ⁺ 24.2 (6 β H) 17 G (1 β H) 6 G (1 β H) 4 G (1 H or ¹⁹ F) e = 2.0029	128 K CH ₃ COH[OĊHC(CH ₃) ₃] ⁺ 22.5 G (1 αH) 138 K
2,2-dimethylpropyl-1,1-d ₂ acetate	31.7 G (3 H) g = 2.0038	133 K $CH_3COH[OCD_2C(CH_3)_2(\dot{C}H_2)]^+$ 21.0 G (2 α H) g = 2.0025	138 K CH ₃ COCD ₂ H[OCH ₂ C(CH ₃) ₂] ⁺ 24.3 G (6 βH) 14.0 G (1 βH) 11.8 G (1 βH) 5 G (1 H or ¹⁹ F) $\alpha = 2.0027$	
2,2-dimethylpropyl-1,1-d ₂ acetate-d ₃	31.2 G (3 H) g = 2.0037	131 K CD ₃ COH[OCD ₂ C(CH ₃) ₂ (ĊH ₂)] ⁺ 21.5 G (2 αH)	g = 2.0027 140 K CD ₃ COCD ₂ H[OCH ₂ Ċ(CH ₃) ₂] ⁺ 24.3 G (6 β H) 149 K 14 G (1 β H) 11 G (1 β H) 5.5 G (1 H or ¹⁹ F) z = 2.0027	
neopentyl propionate	35 G (3 H)	93 K C ₂ H ₃ COH[OCH ₂ C(CH ₃) ₂ (ĊH ₂)] ⁺ 21 G (2 αH) 108 K	g = 2.0027 148 K $C_2H_3COCH_3[OCH_2\dot{C}(CH_3)_2]^{+b}$	148 K CH ₃ ĊHCOH(OR) ^{+c} 25 G (3 βH) 133 K/93 K ^d 22 G (1 αH)
2,2-dimethylpropyl-1,1-d ₂ propanoate	31.6 G (3 H) g = 2.0032	g = 2.0025 115 K C ₂ H ₃ COH[OCD ₂ C(CH ₃) ₂ (ĊH ₂)] ⁺ 22 G (2 α H) 143 K	150 K $C_2H_3COCD_2H[OCH_2\dot{C}(CH_3)_2]^+$ 24.7 G (7 β H) 153 K	150 K CH ₃ ĊHCOH(OR) ^{+c} 24.6 G (3 βH) 156 K/103 K 22 G (1 αH)
		g = 2.0025	g = 2.0027	$g_{\rm av} = 2.0029$

^a The temperature at the head of each entry is that at which a significant concentration of the radical first appears in the ESR spectrum. The temperature next to the hyperfine parameters is that at which the parameters are measured, if different. ^b This radical was identified by comparison of its spectrum with the analogous radical in deuterated neopentyl propionate. Independent hyperfine couplings could not be extracted. ^c The identity of the R group is uncertain. ^d Annealing temperature/temperature of spectrum used to determine hyperfine couplings and g values.



Figure 2. (a) First-derivative ESR spectrum of a frozen solution of 2,2-dimethylpropyl-l, l- d_2 acetate in CFCl₃ after γ -irradiation and measurement at 77 K, due to the cation. (B) Spectrum after annealing to 133 K, due to I. The two outermost lines are due to residual cation at this temperature. (C) Spectrum after annealing to 138 K, due to IIIB (D) Isotropic simulation of spectrum (C) using parameters given in Table I.

has a fully deuterated methylene group and acid methyl group, the spectra are assigned to radical(s) I ($R = -CH_3$ or $-CD_3$).



Upon further warming to approximately 140 K an irreversible change occurs in the spectra (Figures 2C and 3C). These spectra

are the same for both B and C except that the methyl deuterated compound spectrum has slightly narrower line widths and different line intensities in places. The similarity of the two spectra allow us to conclude that the hydrogens on the acid methyl group do not contribute substantial hyperfine coupling to the radical. A simulation of the spectrum in Figure 2C is shown in Figure 2D. This simulation, which agrees with the experimental spectrum quite well, employed isotropic couplings of 24.3 G (6 H), 14.0 G (1 H), 11.8 G (1 H), and 5 G (1 H or ¹⁹F). These results indicate that the radical(s) present at 140 K are IIIB and IIIC.



The fact that B and C (and as shown below, A also) yield identical spectra for III and that all eight major couplings are accounted for strongly support this assignment. The couplings of the newly formed methylene group are reasonable for two β -protons with slightly different dihedral angles of near 60° relative to the singly occupied p orbital. The 24.3-G couplings are typical of rotating methyl groups in hydrocarbon radicals.

There is a question regarding the origin of the 5-G coupling. This coupling is present in all of the radicals III; its origin is somewhat clarified by discussing IIIC. Even though the parent ester C has nine hydrogens, only eight of them are adjacent to the radical site in radical IIIC. The coupling must therefore be due to the ninth proton or to the matrix. We cannot, on the basis of our data, conclude definitively whether the coupling is an ¹⁹F matrix coupling or a coupling with the ninth hydrogen, located on the acetal methyl group. Small (4–5 G) matrix couplings to cation radicals have been observed, as has a small coupling to a distant hydrogen in a radical similar to IIIC.^{3,11,12}



Figure 3. (A) First-derivative ESR spectrum of a frozen solution of 2,2-dimethylpropyl- $1,1-d_2$ acetate- d_3 in CFCl₃ after γ -irradiation and measurement at 77 K, due to the cation. (B) Spectrum after annealing to 131 K, due to I. The two outermost lines are due to residual cation at this temperature. (C) Spectrum after annealing to 149 K, due to IIIC.

The spectra of the undeuterated neopentyl acetate samples were similar to those of the deuterated analogues, but differed in three respects. First, as the sample was annealed, the cation radical persisted until 128 K, at which point the spectrum in Figure 1B was observed. The spectrum here is predominantly a doublet; the most reasonable choice for the radical present is II. This radical persists until the softening point of the matrix, although other radicals are also formed. It is not observed in the deuterated samples probably due to a primary isotope effect which prevents the reaction from occurring. As the temperature is further increased to 141 K, the spectrum shown in Figure 1C is observed. A simulation of the spectrum in Figure 1C is presented in Figure 1D. This simulation, which matches the experimental spectrum quite closely, used couplings of 24.2 (6 H), 16.8 (1 H), 6.1 (1 H), and 4.1 G (1 H). The radical involved is evidently IIIA, analogous to the final radical IIIB and IIIC observed for the deuterated compounds. Thus, unlike the deuterated analogues, no intermediate similar to I was observed.

Finally, as the temperature is further increased, a number of additional small couplings appear. These couplings did not appear in the deuterated samples. We could not definitively interpret these additional couplings, although it is possible that they arise from the $-OCH_3$ group in radical IIIA.

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The proposed reactions of the neopentyl acetate radical cations (excluding the formation of II) are shown in reaction 4. The



 $R=-CH_3 \text{ or } -CD_3$



bracketed species is not observed but, in analogy with the deuterated structures, is almost certainly formed as an intermediate.

We note that, unlike neopentyl formate⁶ (Table III), there is no hint in the ESR spectra that the isobutene cation radical is formed with the acetates. It appears that, in these compounds, cleavage of the C-C(CH₃)₃ bond does not occur as easily as in the formates. Instead, proton transfer from a methyl group on the neopentyl moiety to another site on the molecule occurs first. In the undeuterated molecule, the proton transfer is immediately followed by attack at the carbonyl ("tail biting") and radical IIIA results. For the methylene deuterated compounds, the cleavage of the C-C(CH₃)₃ bond is further suppressed, and the protontransfer intermediate(s) I are observed over a very short temperature range. This is followed by alkyl attack at oxygen, similar to that indicated in reaction 3 for ethyl formate.

Neopentyl Propionate. Neopentyl propionate (D) and one



deuterated analogue 2,2-dimethylpropyl- $1,1-d_2$ propanoate (E) were investigated in this work. The spectra resulting from γ -irradiation of CFCl₃ solutions of D and E at 77 K are shown in Figures 4A and 5A. Both samples give the typical four-line spectra due to a neopentyl ester cation radical.

The spectra due to the deuterated sample are more easily interpreted and are discussed first. At 115 K, the cation diminishes in intensity with a concomitant increase in a 1:2:1 22-G triplet characteristic of a radical with a rotating $-CH_2$ group and is assigned to IV; the spectrum of this radical at 143 K is shown in Figure 5B. Further warming to 150 K results in the conversion of the spectrum of the RCH₂ radical to a complex spectrum (Figure 5C), which is due to two radicals. The spectrum consists principally of an octet on which is superimposed a quintet. The octet, with 24.7-G couplings, is assigned to radical V, which is



formed by alkyl attack at oxygen. The quintet, with ca. 24-G coupling and noticeable anisotropy in the wings, is most reasonably explained by VI. Both of these are formed simultaneously at 150 K. As the temperature is further increased to 155 K, the spectrum due to V disappears while the quintet due to VI remains (Figure 5D). The spectra of the protiated neopentyl propionate sample as it is annealed show the appearance, at 93 K rather than at 115 K, of the RCH₂ hydrogen-transfer radical—Figure 4B shows the spectrum of this radical at 108 K. The spectra at still higher temperatures, while less clear than those of the deuterated compound, indicate that the same reactions occur as did for the

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Figure 4. (a) First-derivative ESR spectrum of a frozen solution of neopentyl propionate in CFCl₃ after γ -irradiation and measurement at 77 K. The components of interest are the typical four broad lines due to the cation (See text). (B) Spectrum after annealing to 108 K, due to the protiated form of IV. (C) Spectrum after annealing to 133 K, measurement at 93 K. The spectrum, due to the protiated form of VI, is taken at the colder temperature in order to broaden (and thereby decrease) background signals due to matrix radicals. There still remains a small background signal in the downfield portion of the spectrum (to the left).



Figure 5. (A) First-derivative ESR spectrum of a frozen solution of 2,2-dimethylpropyl- $1,1-d_2$ propanoate in CFCl₃ after γ -irradiation and measurement at 77 K, due to the cation. (B) Spectrum after annealing to 143 K, due to IV. (C) Spectrum after annealing to 153 K. This spectrum is interpreted as being due to two radicals, V which results in an octet and VI which results in a quintet. The octet spectrum is indicated by sticks. (D) Spectrum after annealing to 156 K and measured at 106 K, due to VI only.

deuterated sample and at approximately the same temperatures. The final radical present gives a quintet, similar to that of the deuterated sample. Thus, the only difference found is that deuteration of the methylene group hinders the hydrogen-transfer reaction, but does not hinder the two reactions that follow.

The proposed reactions for neopentyl propionate are as shown in reaction 5. (R' = neopentyl; the two deuterons marked with



an asterisk may be either protons or deuterons).

Neopentyl Butyrate. Neopentyl butyrate and the deuterated analogue, 2,2-dimethylpropyl-1,1-d₂ butanoate, were investigated. At 77 K, in CFCl₃ solutions after γ -irradiation, the ESR spectra of both samples show a predominance of the four-line spectrum observed previously for the neopentyl group cation radical but also indicate a considerable amount of a $-CH_2$ radical site. Annealing of both samples results in complex overlapping spectra which appear to be due to a number of hydrogen abstraction radicals. Although there is some uncertainty regarding the details, it is relevant to note that there is no evidence for alkyl attack at oxygen, and it appears that the hydrogen abstraction upon annealing is rather nonselective.

Butyl Esters. We note that for all of the butyl esters investigated there was no indication that the cation radicals were stable at 77 K. The spectra observed at 77 K were assigned to one or more products resulting from reaction of the primary cation radical. Concentrations of the parent esters were kept low enough so that it can be reasonably assumed that reaction of the cation radical and subsequent reactions are unimolecular. Table II presents the spectral parameters for the butyl esters.

tert-Butyl Acetate and Isobutyl Acetate. Both of these compounds have been the subject of earlier studies.⁴⁻⁶ In this work, we report the structures of the radicals present when these compounds are subject to γ -irradiation at 77 K in a CF₂ClCFCl₂ matrix.

In CFCl₃, the spectra of both isobutyl acetate^{5,6} and *tert*-butyl acetate^{4,6} are due to the isobutene cation radical. Surprisingly, this is even found to be the case at 4.2 K for *tert*-butyl acetate.⁴ The cation radicals are not observed for either compound; the reactions of both cation radicals to isobutene cation radical occurs in an extremely facile manner. We and others have concluded that both *tert*-butyl acetate and isobutyl acetate fragment through the McLafferty rearrangement.

In a CFCl₂CF₂Cl matrix, however, we observe a different type of reactivity. For both compounds, after γ -irradiation at 77 K, there results a spectrum with eight major lines, with each line further split into a poorly resolved doublet (Figure 6A;D). The spectra of the two compounds are essentially identical and due to the same radical, radical VII. An isotropic simulation using



 $R = CH(CO_2H)(NH_2)$

couplings of 23 G (7 H) and 6 G (1 H) fits the spectra quite well (Table II). The fact that both *tert*-butyl acetate and isobutyl acetate form the same radical and the nature of the couplings indicate that the radical present is VII. This radical is similar in structure to those found earlier for the neopentyl esters. For *tert*-butyl acetate, this radical is likely formed from the cation

TABLE II: Isotropic Hyperfine Couplings and g Values for Butyl Esters^a

ester	matrix	hydrogen-transfer radical	alkyl attack radical	
tert-butyl acetate ^b	CF ₂ ClCFCl ₂		CH ₃ COH[OCH ₂ \dot{C} (CH ₃) ₂] ⁺ 23.1 G (7 β H) 6 5 G (1 β H)	
isobutyl acetate ^b	CF ₂ ClCFCl ₂	CH ₃ COH[OCH ₂ \dot{C} (CH ₃) ₂] ⁺ 23.0 G (7 β H) ~6 G (1 β H) g = 2.0026		
n-butyl formate ^c	CFCl3		HCOH[OC(CH ₃)(C ₂ H ₅)] ⁺ 32.7 G (1 β H) 22.0 G (3 β H) 11.0 G (1 β H) g = 2.0026	
<i>sec</i> -butyl formate ^c	CFCl3	HCOH $[O\dot{C}(CH_3)(C_2H_5)]^+$ 32.7 G (1 β H) 22.0 G (3 β H) 11.0 G (1 β H) g = 2.0026	č	

^a All measurements are at 77 K. ^b tert-Butyl and isobutyl acetate yield the same radical. ^cn-Butyl and sec-butyl formate yield the same radical.

radical by hydrogen transfer followed by alkyl attack at the carbonyl oxygen.



Isobutyl acetate can form the same radical simply by hydrogen transfer from the tertiary carbon. However, we cannot eliminate the possibility that the radical is formed due to hydrogen transfer followed by alkyl attack at the carbonyl and a 1,2-hydrogen shift on the alkyl group.

The identification of this radical is supported by the couplings reported for a similar radical in irradiated leucine.^{13,14} In this case, the radical formed is VIII. The couplings reported for this radical at 300 K are 25 (7 H) and 5 G (1 H), which are close to those we observe for VII. The radical in leucine undergoes a change when cooled to 77 K, at which temperature the 5-G coupling is reported to disappear. We note that the 6-G coupling of the radical in *tert*-butyl acetate disappears when the sample is warmed from 77 to 103 K, and the major coupling increases from 23 to 24 G (Figure 6B). Although the effects of temperature on the hyperfine couplings of the two radicals differ in direction, they both indicate that the radicals involved have more than one conformation easily accessible. It is also relevant that Iwasaki and co-workers observe a spectrum consisting of eight lines at 24-G separation when *tert*-butyl acetate in the same matrix is γ -irradiation at 4.2 K and warmed to 77 K.^{4,15} This is precisely the spectrum that we observe when our sample is warmed from 77 to 103 K.

When warmed to 111 K, VII undergoes conformational and/or motional changes resulting in a spectrum that closely matches the line positions of the spectrum of radical IIIB in deuterated neopentyl acetate. This is not unexpected, since the primary radical site is the same in both radicals and there is one distant hydrogen that can show hyperfine coupling. Upon annealing both the isobutyl and tert-butyl acetate samples to still higher temperatures, there was no clear evidence that VII reacts to form different radicals. The appearance of large background signals due to the CF₂ClCFCl₂ matrix at approximately 123 K preclude further conclusions regarding what occurs at higher temperatures.

n-Butyl and sec-Butyl Formate. After irradiation at 77 K of solutions in CFCl₃, the spectra of n-butyl and sec-butyl formate are the same (Figure 7A,B). An isotropic simulation using couplings of 33 (1 H), 22 (3 H), and 11 G (1 H) agrees well with the experimental spectra (Figure 7C). In order to explain the



Figure 6. (A) First-derivative ESR spectrum of a frozen solution of tert-butyl acetate in CFCl₂CF₂Cl after γ -irradiation and measurement at 77 K, due to VII. The bar corresponds to 20 G. (B) Isotropic simulation of spectrum A using parameters given in Table II. (C) Spectrum after annealing to 103 K, due to a different conformation of VII. The sharp central doublet may be due to a third conformation of the same radical. (D) Spectrum of isobutyl acetate in CFCl₂CF₂Cl after irradiation and measurement at 77 K, also due to VII. The line positions are the same as those in spectrum A. A sharp background doublet is present.

fact that both compounds yield the same spectrum and that there are couplings to five protons, we propose that the radical present is IX. The three couplings of 22 G are somewhat low for methyl group couplings due to the delocalization of spin density from the carbon radical site to the $-CO_2$ - electronic system.

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(14) Snipes, W.; Schmidt, J. Radiat. Res. 1966, 29, 194.
(15) Iwasaki and co-workers tentatively assign this spectrum to CH₃CHCH₃. Our work indicates another intermediate.



The formation of these radicals is consistent with our previous observations. *sec*-Butyl formate likely forms IX by proton transfer to form a secondary radical. *n*-Butyl formate can form this radical through proton transfer to the carbonyl followed by alkyl attack at the carbonyl and a 1,2-hydrogen transfer within the alkyl group.

Neopentyl Formate. Our previous work with neopentyl formate showed that the cation radical was produced at 77 K and that it decayed, through an intermediate, to isobutene cation at 150 K.⁶ The intermediate was identified only as an "RCH₂· radical". There are three reasonable possible mechanisms through which a radical with a $-CH_2$ · site could form from neopentyl formate. The first is by intramolecular hydrogen transfer from one of the methyl groups, as was found for the neopentyl acetates and propionates. A second is the same transfer process and simultaneous (or fast) intramolecular alkyl attack at the carbonyl oxygen with cleavage of the O-CH₂ ester bond; this reaction is similar to those we have described above. A third, which is the one most strongly supported by our ESR evidence, is cleavage of the CH₂-C(CH₃)₃ bond in the ester cation radical to form the -CH₂· site and a *tert*-butyl cation as shown in reaction 7. In this

$$\begin{array}{c} 0 & C(CH_3)_3 & +_0 & -C(CH_3)_3 \\ \parallel & + \parallel \\ \parallel & -_{-}^{C} & -_{-}^{CH_2} \end{array} \xrightarrow{H_1} \begin{array}{c} 0 & -_{-}^{C(CH_3)_3} \\ \parallel & \parallel \\ H_2 & -_{-}^{C} & -_{-}^{CH_2} \end{array} \xrightarrow{H_1} \begin{array}{c} 0 \\ 0 \\ \parallel \\ H_2 & -_{-}^{C} & -_{-}^{CH_3} \end{array} \xrightarrow{H_2} \begin{array}{c} C(H_3)_3 \\ -_{-}^{CH_2} & -_{-}^{CH_2} \end{array} \xrightarrow{H_2} \begin{array}{c} 0 \\ 0 \\ \parallel \\ H_2 & -_{-}^{C} & -_{-}^{CH_3} \end{array} \xrightarrow{H_2} \begin{array}{c} C(H_3)_3 \\ -_{-}^{C} & -_{-}^{CH_2} \end{array} \xrightarrow{H_2} \begin{array}{c} 0 \\ -_{-}^{CH_2} & -_{-}^{CH_3} \end{array} \xrightarrow{H_2} \begin{array}{c} 0 \\ -_{-}^{CH_3} & -_{-}^{CH_3} \end{array} \xrightarrow{H_2} \begin{array}{c} 0 \\ -_{-}^{CH_3} & -_{-}^{CH_3} \end{array} \xrightarrow{H_3} \begin{array}{c} 0 \\ -_{-}^{CH_3} & -_{-}^{CH_3} \end{array} \xrightarrow{H_3} \end{array} \xrightarrow{H_3} \begin{array}{c} 0 \\ -_{-}^{CH_3} & -_{-}^{CH_3} \end{array} \xrightarrow{H_3} \begin{array}{c} 0 \\ -_{-}^{CH_3} & -_{-}^{CH_3} \end{array} \xrightarrow{H_3} \end{array} \xrightarrow{H_3} \begin{array}{c} 0 \\ -_{-}^{CH_3} & -_{-}^{CH_3} \end{array} \xrightarrow{H_3} \begin{array}{c} 0 \\ -_{-}^{CH_3} & -_{-}^{CH_3} \end{array} \xrightarrow{H_3} \end{array} \xrightarrow{H_3} \begin{array}{c} 0 \\ -_{-}^{CH_3} & -_{-}^{CH_3} \end{array} \xrightarrow{H_3} \begin{array}{c} 0 \\ -_{-}^{CH_3} & -_{-}^{CH_3} \end{array} \xrightarrow{H_3} \end{array} \xrightarrow{H_3} \begin{array}{c} 0 \\ -_{-}^{CH_3} & -_{-}^{CH_3} \end{array} \xrightarrow{H_3} \begin{array}{c} 0 \\ -_{-}^{CH_3} & -_{-}^{CH_3} \end{array} \xrightarrow{H_3} \begin{array}{c} 0 \\ -_{-}^{CH_3} \end{array} \xrightarrow{H_3} \begin{array}{c} 0 \\ -_{-}^{CH_3} & -_{-}^{CH_3} \end{array} \xrightarrow{H_3} \end{array} \xrightarrow{H_3} \begin{array}{c} 0 \\ -_{-}^{CH_3} \end{array} \xrightarrow{H_3} \begin{array}{c} 0 \\ -_{-}^{CH_3} \end{array} \xrightarrow{H_3} \end{array} \xrightarrow{H_3} \begin{array}{c} 0 \\ -_{-}^{CH_3} \end{array} \xrightarrow{H_3} \begin{array}{c} 0 \\ -_{-}^{CH_3} \end{array} \xrightarrow{H_3} \end{array} \xrightarrow{H_3} \begin{array}{c} 0 \\ -_{-}^{CH_3} \end{array} \xrightarrow{H_3} \begin{array}{c} 0 \\ -_{-}^{CH_3} \end{array} \xrightarrow{H_3} \end{array} \xrightarrow{H_3} \begin{array}{c} 0 \\ -_{-}^{CH_3} \end{array} \xrightarrow{H_3} \end{array} \xrightarrow{H_3} \begin{array}{c} 0 \\ -_{-}^{CH_3} \end{array} \xrightarrow{H_3} \begin{array}{c} 0 \\ -_{-}^{CH_3} \end{array} \xrightarrow{H_3} \end{array} \xrightarrow{H_3} \begin{array}{c} 0 \\ -_{-}^{CH_3} \end{array} \xrightarrow{H_3} \end{array} \xrightarrow{H_3} \begin{array}{c} 0 \\ \end{array} \xrightarrow{H_3} \end{array} \xrightarrow{H_3} \begin{array}{c} 0 \\ \end{array} \xrightarrow{H_3} \end{array} \xrightarrow{H_3} \begin{array}{c} 0 \\ -_{-}^{CH_3} \end{array} \xrightarrow{H_3} \end{array} \xrightarrow{H_3} \begin{array}{c} 0 \\ \end{array} \xrightarrow{H_3} \end{array} \xrightarrow{H_3} \end{array} \xrightarrow{H_3} \begin{array}{c} 0 \\ \end{array}$$

reaction, the *tert*-butyl cation formed is assumed to associate with the carbonyl oxygen as indicated (see Discussion).

In order to determine which path was correct, we have, in this work, investigated two deuterated analogues of neopentyl formate, 2,2-dimethylpropyl- $1,1-d_2$ formate (F) and 2,2-dimethylpropyl-

$$\begin{array}{c} \circ & \circ & \circ \\ \parallel & & \downarrow \\ H \\ - & \circ \\ - & \circ \\ - & C \\ - &$$

 $1,1-d_2$ formate-d (G). Table III summarizes the results found for these compounds.

In Figures 8A and 9A, we show the spectra found for compounds F and G, respectively, after γ -irradiation of solutions in CFCl₃. The spectra are identical with those previously found for neopentyl formate (undeuterated) except that the line widths are narrower for the deuterated samples; they are clearly due to the ester cation radicals.⁶ The fact that deuteration of the methylene and formyl protons only decreases the line width indicates that these protons have only small hyperfine couplings, less than 5 G.

Figures 8B and 9B show the spectra of the radical that appears in the deuterated samples after annealing to approximately 100 K-the figures show the spectra at higher temperatures where resolution is improved. The dramatic change that has occurred is irreversible, indicating that a reaction has taken place. The spectrum found for F is consistent with couplings from two deuterons at 4.0 G each and one proton at 4.0 G, whereas that found for G shows couplings to two deuterons only at 4.0 G each. The loss of the 4.0-G proton coupling when the formyl proton is deuterated allows an unequivocal assignment of the coupling to the formyl proton. The couplings from the two deuterons must arise from a $-CD_2$ site, analogous to the $-CH_2$ site observed in the undeuterated compound. (A 4-G deuteron coupling corresponds to a proton coupling of 26 G, which is larger than the isotropic coupling typically found for α -protons. This difference is likely due to an incomplete averaging of the anisotropy in the couplings.) These results clearly suggest that fragmentation in



Figure 7. (A) First-derivative ESR spectrum of a frozen solution of sec-butyl formate in CFCl₃ after γ -irradiation and measurement at 77 K, due to IX. (B) Spectrum of *n*-butyl formate under identical conditions. The spectrum is the same as that found for *n*-butyl formate and arises from the same radical. (C) Isotropic simulation of spectra A and B using the parameters given in Table II.

neopentyl formate and its deuterated analogues occurs at the $C-C(CH_3)_3$ bond. Much of the trapped hole in the cation radical is located in this bond; it is therefore weakened and cleaves easily.¹⁰



Radical XA or XB or XC is produced, depending on the initial compound; these radicals are denoted collectively as X.

Further warming of the samples to approximately 150 K results in conversion of the spectra to that of the isobutene cation radical (Figure 8C and 9C and Figure 4C of ref 6); this radical and its ESR spectrum have been unequivocally identified in earlier work.^{4-6,12} We propose that isobutene forms through intramolecular hydrogen abstraction and cleavage of the weak C-O bond as shown in reaction 7. Reaction 7 fully accounts for the spectra observed. The other two possible mechanisms mentioned fail to explain one or more features of the experimental data. For example, the first path (hydrogen transfer from a methyl) is rejected since the deuterated compounds form $a - CD_2$, site, not $a - CH_2$. site. The second path (hydrogen transfer plus alkyl attack) is rejected since an initial $-CH_2$, radical is not observed and because this path would produce a partially deuterated isobutene cation radical ($^+CD_2^-C(CH_3)_2$) which is not observed.¹⁶

⁽¹⁶⁾ The observed isobutene cation radical spectra show no deuterium splittings, nor the anomalous line intensities that might be expected if the spectrum of the partially deuterated form were underlying the protiated form.

TABLE III: Isotropic Hyperfine Couplings and g Values for Neopentyl Formates in $CFCl_3^a$

ester	cation radical (77 K)	tert-butyl cation-transfer radical	isobutene cation radical
neopentyl formate ^b	33 G (3 H) g = 2.0032	100 K HCOĊH ₂ [OC(CH ₃) ₃] ⁺	150 K +•CH ₂ •C(CH ₃) ₂
	Ũ	23 G (2 αH) ^c 4.0 G (1 H)	14.8 G (8 H)
		98 K	147 K
2,2-dimethylpropyl- $1,1-d_2$ formate	31.8 G (3 H)	$HCOCD_2[OC(CH_3)_3]^+$	$+\cdot CH_2 - C(CH_3)_2$
	g = 2.0033	4.0 G (2 αD) 133 K 4.0 G (1 H)	14.7 G (8 H) 150 K
		g = 2.0025	g = 2.0026
2,2-dimethylpropyl-1,1-d ₂ formate-d	32 G (3 H)	103 K	148 K
		$DCOCD_2[OC(CH_3)_3]^+$	$+CH_2-C(CH_3)_2$
		4.0 G (2 αD) 118 K	14.7 G (8 H) 153 K
		g = 2.0025	g = 2.0026

^a Please refer to note a, Table I for explanation of temperatures. ^b Reference 6. ^c This spectrum shows α anisotropic structure which was analyzed in part in ref 6. This current work clarifies the presence of a 4.0 G coupling to the formate proton in the spectrum.





Figure 8. (A) First-derivative ESR spectrum of a frozen solution of 2,2-dimethylpropyl- $1,1-d_2$ formate in CFCl₃ after γ -irradiation and measurement at 77 K, due to the cation. (B) Spectrum after annealing to 133 K, due to XB. (C) Spectrum after annealing to 150 K. This spectrum is due to isobutene cation radical.

Summary and Conclusions

Both from this present work and earlier work, it is clear that ester cation radicals are inherently reactive species. Of the many esters investigated thus far, the only ester cations stabilized at 77 K are those of the neopentyl esters, and in these cases the unpaired spin and charge is located largely on the neopentyl group. The neopentyl ester cations thus resemble neopentane cation rather than ester cations. It is clear that a large spin density in the ester functional group, as presumably occurs for the smaller less stable ester cations, potentiates the proton or H transfer in these species. Whether it is actually a proton or hydrogen that transfers seems moot. Due to the delocalized nature of charge in ester cations, the transferring species is likely a somewhat positively charged

Figure 9. (A) First-derivative ESR spectrum of 2,2-dimethylpropyl-1,1-d₂ formate-d in CFCl₃ after γ -irradiation and measurement at 77 K, due to the cation. (B) Spectrum after annealing to 118 K, due to XC. (C) Spectrum after annealing to 153 K, arising from isobutene cation radical. Some of the radical causing spectrum B remains.

hydrogen. We have used the term "hydrogen transfer", but do not mean to imply that a neutral hydrogen atom is actually the entity that moves.

In this work we have proposed two new solid-state reaction mechanisms that Freon matrix isolated ester cation radicals may undergo at cryogenic temperatures. One is hydrogen transfer followed by intramolecular alkyl attack at oxygen. The other, which we have proposed for neopentyl formate only, is carboncarbon bond cleavage accompanied by intramolecular *tert*-butyl cation transfer. These two new reactions and those found in earlier work are illustrated in Figure 10.

There remains some ambiguity about the details of the neopentyl formate reaction which merits some comment. While the evidence confirming the occurrence and site of carbon-carbon bond

⁽¹⁷⁾ Shida, T.; Haselbach, E.; Bally, T. Acc. Chem. Res. 1984, 180.



Figure 10. Schematic representation of the reactions of ester cation radicals in frozen Freon matrices. This figure shows the reaction paths we have observed for a variety of esters. Hydrogen transfer refers to intramolecular movement of a hydrogen or proton (see Discussion) from carbon to oxygen; hydrogen abstraction is an inter- or intramolecular movement from one carbon to another. The reader is cautioned that this is a representative schematic. Not all reactions are shown for all possible ester structures we have investigated. The reactions that do occur are dependent, among other things, on temperatures, solvent, extent and location of deuteration, ester concentration, and specifics of ester structure. Reference 1-7 should be consulted for details.

cleavage is unambiguous, the disposition of the *tert*-butyl cation formed as a result is a matter of conjecture. We feel certain that an isolated *tert*-butyl cation would not be stable in the solid state and that it must associate either with the matrix or intramolecularly with a new site on the ester cation radical. The matrix used is known to stabilize cations, but given the fact that a reaction later occurs between the *tert*-butyl cation and the $-CH_2$ radical site, we infer that intramolecular association occurs.

The nature of the association of the *tert*-butyl cation with the ester structure is also a matter of conjecture. Without any evidence to the contrary, we felt it reasonable to argue by analogy to the hydrogen-transfer reactions that have been found in ester cation radicals. Thus, it is presumed that there is a weak dative bond formed between the carbonyl oxygen and the positively charged tertiary carbon in *tert*-butyl cation.

The alkyl attack on oxygen, which we have described, is an intramolecular free radical attack in which a primary free radical rearranges to a more stable tertiary free radical. A 1,4-hydrogen shift accompanies the attack, which may occur in a concerted fashion through a bicyclic transition state with a bridging hydrogen (reaction 8).



We find it interesting to note that for the neopentyl esters we have not observed any further reaction of the rearranged tertiary radical. Thus, formation of the rearranged radical and fragmentation seem to be mutually exclusive paths under the conditions of our experiments. The cations of isobutyl acetate and tert-butyl acetate rearrange to the tertiary radicals in CF₂ClCFCl₂ but fragment in CFCl₃. CF₂ClCFCl₂ forms a glass, and it appears that the solid-state solvation of the original cation prevents fragmentation, whereas the more open structure of the crystalline CFCl₃ allows fragmentation to occur. The open structure of the CFCl₃ appears to be part of the "rotator solid"¹⁷ phenomenon that results in efficient motional averaging of the anisotropic interactions in the solid state. We have no evidence for isobutyl and tert-butyl acetate whether we are observing two mutually exclusive solvent-dependent reaction paths, or different stages of one pathway.

Of equal interest is the change in reaction that occurs for the neopentyl esters as the acyl R group is changed. Neopentyl formate fragments (through an intermediate) with no proton transfer, the acetate and propionate undergo proton transfer followed by intramolecular alkyl attack at oxygen, and the butyrate shows evidence for proton transfer but no evidence for intramolecular alkyl attack. The thermodynamic data necessary to fully understand these changes are not available. However, the transition state suggested above does help to rationalize some of our findings. For neopentyl formate cation radical, the greatly weakened C-C(CH₃)₃ bond cleaves and C(CH₃)₃⁺ migrates to oxygen; the transition state is not involved. When the acyl group CH_3 or C_2H_5 is present, the increased electron-donating ability of the group strengthens the $C-C(CH_3)_3$ bond in the cation radical, thereby preventing fast cleavage and simultaneously stabilizing the suggested transition state, which possesses a highly delocalized positive charge. Thus, intramolecular alkyl attack occurs. The still larger acyl C_3H_7 encourages hydrogen loss for the acyl portion of the cation, perhaps through a variety of five- and six-membered ring intermediates which effectively compete with the alkyl attack pathway.

This work indicates that the alkyl attack at oxygen is an important potential reaction path for the hydrogen-transfer radical derived from ester cation radicals. The reaction is not directly observable through mass spectroscopic investigation since the charge/mass ratio of the cation is not changed. In ester cation radicals with symmetric ester moieties (such as ethyl formate) but asymmetric environments, the reaction may occur and be undetectable even by standard ESR techniques. Yet, since in most cases the product formed is chemically different than the reactant, this reaction may determine the overall reaction sequence of the ester cation radical involved. Given the propensity for this reaction to occur even at 77 K, it would not be surprising to find that a significant fraction of the ions responsible for the molecular ion peak in a mass spectrum of an ester are in this rearranged form.

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