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ABSTRACT

The products formed in the irradiation of liquid isopropyl acetate and isopropenyl acetate with helium ions have been studied at room temperature and at 80°C. The reduced products are formed in lower yield in isopropenyl acetate than in isopropyl acetate by a factor of about three. A factor-of-thirty higher "polymer" yield from isopropenyl acetate indicates that radicals, which in isopropyl acetate are used for reduced product production, are used for polymer production in isopropenyl acetate by addition to the double bond. A discussion of possible reaction mechanisms for various products is given.

THE RADIATION CHEMISTRY OF ISOPROPYL ACETATE AND ISOPROPENYL ACETATE

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INTRODUCTION

The effects of radiation on isopropenyl acetate is of considerable interest because it is an unsaturated compound which does not readily polymerize to a high-molecular-weight polymer, either under the influence of radiation or by chemical means. For this reason it is also a good compound to use in comparing the effects of a double bond on the radiolytic activity of a molecule containing other electro-negative groups. Therefore, we have studied the radiolysis products resulting from the helium-ion irradiation of isopropyl acetate and isopropenyl acetate.

EXPERIMENTAL

Materials used: Eastman (white label grade) isopropyl acetate and isopropenyl acetate were purified by the method of Haggerty and Weiler.[1] Each was finally

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(1) Haggerty, C. J. and Weiler, J. F., J. Amer. Chem. Soc. 51, 1623 (1929).

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distilled through a 25-plate adiabatic column. Refractive index and mass-spectrometer pattern coefficients of samples taken during the distillation showed no change during the middle half of the distillation, and the first and last quarters were discarded. The properties of the purified materials are shown in Table I. When the purified isopropenyl acetate was run in a blank determination, using the same method of separation of low-boiling components as in the product determinations, the following impurities were detected in molal parts per million: Toluene - 1.3 ppm, benzene - 14.5 ppm, methyl ethyl ketone - 73 ppm, and acetone - 51 ppm. With the impurities which appear as products, the amount of impurity has been subtracted in calculating

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                    San Francisco, California

the yield in each case. In view of the apparently high dependence of acetone yield on energy input described later, this procedure is possibly open to some question.

Analytical Methods.

The gases and low-boiling products were separated by refluxing the material under vacuum, as previously described.[2] In this way, samples volatile at -196°,

(2) Newton, A. S., Analytical Chem. 28, 1214 (1956).

-125°, -80°, and also a distilled liquid fraction not rapidly volatile at -80° were collected and analyzed with a Consolidated Engineering Corp.[1] model 21-103 mass spectrometer. Checks on the residual liquids by gas chromatographic methods showed no products of boiling point less than about 150°, other than those listed in Table II, to be present in appreciable yield. "Polymer" was determined by vacuum evaporation of the residual liquid and weighing of the resultant product; molecular weights were determined by the freezing-point depression of benzene. Acid was determined by titration with alcoholic sodium hydroxide to a phenol-phthalein end point. No acid was found in the isopropenyl acetate bombardments by titration, as titration to the end point required less sodium hydroxide for the irradiated material than the small blank of the unirradiated material. Gas chromatograms showed acetic acid to be formed, but quantitative measurements were not possible. Water was determined, but the values were very erratic in both esters by the Karl Fischer method, and the yields, if any, were small.

Irradiations were made in glass cells of the type described by Garrison, Haymond, and Weeks[3] except for the highest energy input irradiation of isopropyl acetate, which was made in the metal target described previously.[4] All samples were thoroughly degassed before irradiation.[2]

(3) Garrison, W. M., Haymond, H. R., and Weeks, B. M., Radiation Research 1, 97 (1954).

(4) McDonell, W. R. and Newton, A. S., Nucleonics 10-1, 62 (1952).

The irradiations at 80°C were made by preheating the cells in an oven at 80° and heating with an infra red lamp, calibrated with respect to distance and voltage to maintain the temperature, during the irradiation.

The experimental results of irradiation at four energy-input levels on isopropyl acetate and two energy-input levels on isopropenyl acetate are shown in Table II, and the effect of a change of temperature from 25° to 80° for each of the acetates is shown in Table III.

DISCUSSION

Effect of Total Energy Input.

Except for the products acetaldehyde and acetone, there is little change in the yields of products from either of these esters in the range of energy input studied. Therefore, for most products, the differential yield of product and the observed yield of product are the same at any energy input in this range. This implies both a lack of secondary products and a lack of action of primary products as radical or excitation scavengers. For the products acetone and acetaldehyde where appreciable effects of energy input were observed, the reactions leading to the lowering of the yields of these products do not lead to appreciably higher yields of carbon monoxide, methane, and ethane, as was observed in the case of isopropyl ether irradiations.[5] This difference in behavior implies a different type mechanism may

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(5) Newton, A. S., U.S.A.E.C. Report No. UCRL-3699. "Some Aspects of the Radiation Chemistry of Isopropyl Ether." Presented at 131st meeting American Chemical Society, Miami, Fla., April 8, 1957. Submitted to J. Phys. Chem., May, 1957.

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be operative in reducing the yields of these products than was postulated for the case of isopropyl ether.

Hydrogen and Hydrocarbon Yields.

The most obvious difference between the radiolytic activity of isopropyl acetate and that of isopropenyl acetate is the decrease by a factor of three in the yields of hydrogen and hydrocarbon products and an increase by a factor of about thirty in the polymer yield, when the double bond is present, over the yield when it is absent. A comparison of hydrogen and corresponding hydrocarbon products for the two compounds in Table IV shows the relative distribution of hydrocarbon compound types to be similar, suggesting similar mechanisms for their formation in the two respective cases, with the differences in yield resulting from differences in the processes competitive to those yielding the hydrocarbon products and hydrogen. There are several unusual features of this distribution. First is the very high yield of C_4 hydrocarbon of the type $R\,CH_3$ compared to the C_3 hydrocarbons of the type RH where R is the isopropyl or isopropenyl group, respectively. It seems unlikely that the isobutane and isobutene from the respective starting compounds could be formed in such large yields (compared to propane and propene yields respectively) by competitive radical reactions between isopropyl and
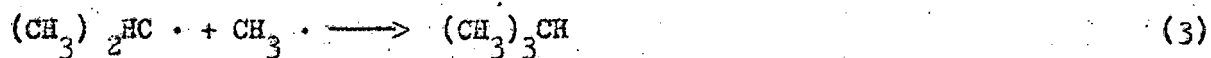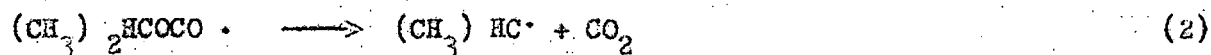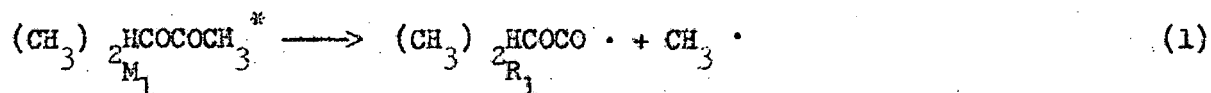
isopropenyl radicals, respectively, and methyl radicals. Therefore, a process such as suggested previously for a similar yield distribution in the tert-butyl ethers[6]
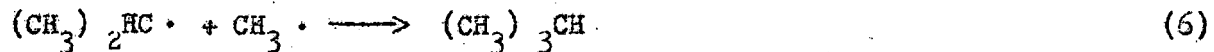
(6) Newton, A. S., UCRL-3694 "A Survey of the Radiation Chemistry of Some Aliphatic Ethers." Presented at 131st meeting American Chemical Society, Miami, Fla., April 8, 1957. Submitted to J. Phys. Chem., May, 1957.

appears an attractive possibility. In this process as applied to isopropyl acetate, an effective methyl rearrangement is achieved by a rapid sequence of steps 1 to 3 before the radicals are separated by diffusion. The equations as written for isopropyl acetate also apply to isopropenyl acetate leading to isobutene in step (3).

$$(CH_3)_2HCOCOCH_3^{*}_{M_1} \longrightarrow (CH_3)_2HCOCO \cdot_{R_1} + CH_3 \cdot \tag{1}$$

$$(CH_3)_2HCOCO \cdot \longrightarrow (CH_3)HC \cdot + CO_2 \tag{2}$$

$$(CH_3)_2HC \cdot + CH_3 \cdot \longrightarrow (CH_3)_3CH \tag{3}$$

In this case there is the alternative process in the sequence of reactions shown in equations (4), (5), and (6). These must also follow in rapid order if the radicals are not to be separated by diffusion.

$$M_1^{*} \longrightarrow (CH_3)_2HC \cdot + CH_3COO \cdot \tag{4}$$

$$CH_3COO \cdot \longrightarrow CH_3 \cdot + CO_2 \tag{5}$$

$$(CH_3)_2HC \cdot + CH_3 \cdot \longrightarrow (CH_3)_3CH \tag{6}$$

No absolute decision is possible from the present data as to the direction for the rearrangement, but Steacie[7] agrees to the assignment of a high activation energy for

(7) E. W. R. Steacie, "Atomic and Free Radical Reactions," Reinhold Publishing Co., New York, 2nd Edition, 1954, Vol. II, p. 596.

the dissociation of the acetate radical, making reaction (5) rather unlikely as an intermediate step, in view of the rapid time sequence required.

The yield of propene (of some five times that of propane from isopropyl acetate) and that of propyne plus propadiene (of some six times that of propene from isopropenyl acetate) cannot occur by a competitive radical process. A rearrangement similar to that postulated for the formation of alkenes from alcohols,[8] ethers,[6] and alkyl halides[9] is a possible mechanism in these cases.
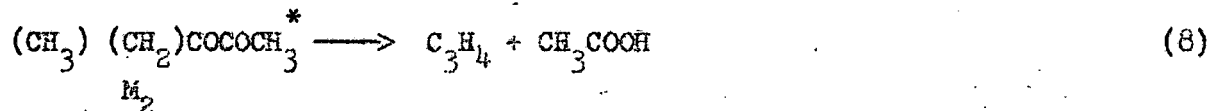
(8) McDonell, N. R., and Newton, A. S., J. Am. Chem. Soc., 76, 4651 (1954).

(9) Hornig, E. O., and Willard, J. E.; and Hanhrahan, R. J., and Willard, J. E., private communication from J. E. Willard (In press, J. Amer. Chem. Soc. 1957).

$$M_1^* \longrightarrow C_3H_6 + CH_3COOH \tag{7}$$

$$\underset{M_2}{(CH_3)(CH_2)COCOCH_3^*} \longrightarrow C_3H_4 + CH_3COOH \tag{8}$$

In the case of isopropyl acetate, the yield of acid was approximately equal to the yield of propene, lending support to the mechanism postulated. No acid was determined from isopropenyl acetate, but difficulties in titration (isopropenyl acetate decomposes vigorously in even slightly basic solution) cast some doubt on any negative chemical test. Acetic acid was observed in the gas chromatogram of the residual liquid from isopropyl acetate irradiations.

Oxygenated Products.

The oxygenated products formed are carbon monoxide, carbon dioxide, acetone, acetaldehyde, and in the case of isopropyl acetate, methyl isopropyl ether and acetic acid. The production of the latter compound has already been considered in connection with propene production. Only possible traces of methyl isopropenyl ether were found in isopropenyl acetate irradiations. A small yield of isopropenyl acetate was found in the products of the irradiation of isopropyl acetate by gas chromatographic analysis of the residual liquid.

Possible reactions leading to the oxygenated products from isopropyl acetate are:

$$\underset{R_1}{M_1^*} \longrightarrow (CH_3)_2 HCO \cdot + CH_3CO \cdot \tag{9}$$

$$CH_3CO \cdot \longrightarrow CH_3 \cdot + CO \tag{10}$$

$$R_1 \longrightarrow CH_3COCH_3 + H \cdot \tag{11}$$

$$R_1 \longrightarrow CH_3CHO + CH_3 \cdot \tag{12}$$

$$R_1 + R \cdot \longrightarrow CH_3 COCH_3 + RH \tag{13}$$

$$R_1 + CH_3 \cdot \longrightarrow (CH_3)_2HCOCH_3 \tag{14}$$

$$M_1^* \longrightarrow CH_3COCH_3 + CH_3CHO \tag{15}$$

These reactions account in an approximate manner for the yield of these products produced. Reaction (15) must have a yield of less than $G = 0.65$, it being limited by the acetone yield, and some acetone must also be produced by reactions (11) and (13). Therefore, to account for the acetaldehyde yield, reaction (12) must have a yield of something greater than one, as must reactions (9) and (10). Reaction (14) has a yield of about 0.26, as determined by the methyl isopropyl ether yield, putting a minimum yield on reaction (9) of 1.26 to account for reactions (12) and (14). Therefore, the yield of CO and methyl radicals from reaction (10) should be about 1.26, while the CO yield observed is 1.17. The total methyl radical yield is therefore about 2.26, of which 0.26 is used in reaction (14). The sum of methane and twice ethane is 2.08. Some methyl radicals will be produced by reaction (5) if it occurs in this system.

Reaction (2) accounts for a G value for carbon dioxide of only 0.25, while the observed yield is about 0.75. It is difficult to account for the carbon dioxide because of the relatively low yield of propane and isobutane. Isopropyl radicals must be formed as a co-product of any obvious mechanism of CO_2 formation, whether by reaction sequences (1) and (2) or (4) and (5). Some propylene could arise from propyl radicals by the hydrogen-abstraction reaction (16),

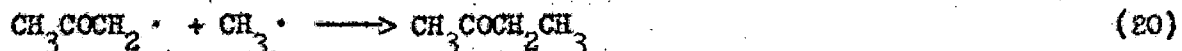$$i-C_3H_7 \cdot + R \cdot \longrightarrow C_3H_6 + RH, \tag{16}$$

but it is doubtful if this can be made to account for the observed lack of products related to propyl radicals.

The oxygenated products from isopropenyl acetate are characterized by very high yields of carbon monoxide and acetone, with a lower yield of acetaldehyde and
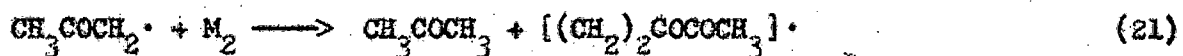
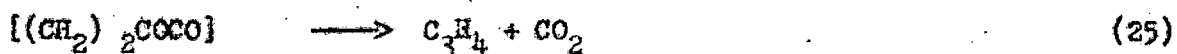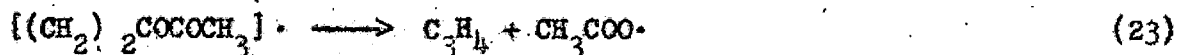carbon dioxide. Thus, reactions (17) and (18) must be almost predominant.

$$M_2^* \longrightarrow \underset{R_2}{(CH_3)(CH_2)} CO\cdot + CH_3CO\cdot \tag{17}$$

$$CH_3CO\cdot \longrightarrow CH_3\cdot + CO \tag{18}$$
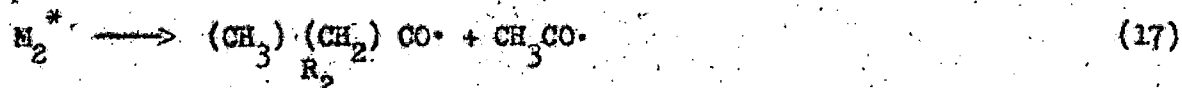
The fate of the isopropenyloxy radical is not completely certain, but most of it must end up as acetone. The isopropenyloxy radical, R_2, must rearrange immediately to the more stable acetonyl radical, which on reaction with methyl radicals leads to methyl ethyl ketone. The rapid rearrangement of this radical is probably the reason no methyl isopropenyl ether is formed as a product.

$$(CH_3)(CH_2) CO\cdot \longrightarrow CH_3COCH_2\cdot \tag{19}$$

$$CH_3COCH_2\cdot + CH_3\cdot \longrightarrow CH_3COCH_2CH_3 \tag{20}$$

The yield of acetone is not consistent with the yield of other co-products. If the acetonyl radical can abstract hydrogen from a molecule of isopropenyl acetate, which would provide an additional source of acetone:

$$CH_3COCH_2\cdot + M_2 \longrightarrow CH_3COCH_3 + [(CH_2)_2COCOCH_3]\cdot \tag{21}$$

$$CH_3CO\cdot + CH_3\cdot \longrightarrow CH_3COCH_3 \tag{22}$$

Reaction (22) is in competition with carbon monoxide production by dissociation of the acetyl radical. The fate of the radical product in reaction (21) is not known. If it is unstable, it could break up by two paths, both of which lead to propyne or propadiene and to carbon dioxide and methyl radicals.

$$[(CH_2)_2COCOCH_3]\cdot \longrightarrow C_3H_4 + CH_3COO\cdot \tag{23}$$

$$\longrightarrow [(CH_2)_2COCO] + CH_3\cdot \tag{24}$$

$$[(CH_2)_2COCO] \longrightarrow C_3H_4 + CO_2 \tag{25}$$

Relative Reactivity.

A comparison of the products from the two esters shows that while there is apparently less reactivity in the isopropenyl acetate if only the gaseous products are considered,   the overall reactivity is higher for isopropenyl acetate than for isopropyl acetate, if the polymer is included. The composition of the isopropenyl acetate "polymer" is not known, but from the average molecular weight, it corresponds to the polymerization of 3 to 4 molecules of the ester before the chain is discontinued.

The low yield of products from isopropenyl acetate formed through radical intermediates, e.g., H_2, CH_4, C_2H_6, etc., can certainly be attributed to the action of the double bond in isopropenyl acetate as a radical scavenger. The low molecular weight of the resulting polymer indicates the chain length of the resulting polymerization

$$M_2 + R \cdot \longrightarrow [(CH_3)(CH_2R)\underset{R_3}{COCOCH_3}] \cdot \qquad (26)$$
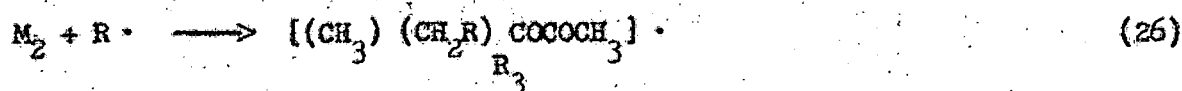
to be limited to one or two further additions of isopropenyl acetate. This chain length can be short if the activation energy for subsequent additions of the monomer is high or if the steric factors are unfavorable, resulting in a long life for R_3 or its first or second addition product. A check for free radicals in the "polymer" from isopropenyl/acetate/which had never been exposed to air showed no free radicals in concentration greater than 10^{-5} M in the concentrated liquid polymer, using a paramagnetic resonance spectrometer. This measurement was made two days after irradiation, and the lack of radicals of mean life longer than a fraction of a day shows the polymerization is probably not stopped by the formation of "buried" radicals.

Therefore, the preferred reaction of R_3 or its immediate descendant may be to form (a) a high-molecular-weight diester or triester through dimerization of radicals, or (b) a high-molecular-weight monoester by reaction with another radical, or (c), to disproportionate to form a saturated and an unsaturated ester. Such expected products were not seen in appreciable yields in gas chromatograms of the residual liquid.

A comparison of the products from the two respective molecules shows that, in each, the most reactive bond is that between the alkoxy group and the acetyl group. The relative yields of oxygenated products which result from the cleavage of this bond are higher by a factor of two or three than those resulting from the cleavage of the alkyl-acetate bond.

Effect of Temperature.

The effect of a 55° rise in temperature at which the compounds were irradiated produced a general rise in product yields consistent with the concept of less recombination of the primary radicals to reform the original material at the higher temperature. The increase is least for the products acetaldehyde, acetone, and methyl isopropyl ether; the first two compounds showed small temperature coefficients from isopropyl acetate, whereas that of the ether was negative. Both acetone and acetaldehyde showed negative temperature coefficients from isopropenyl acetate. These changes can be attributed, at least in part, to the greater attack by radicals on these products at the higher temperatures, and, in part, to their production from unstable intermediates which decay more rapidly at the higher temperature to yield other products. Thus from isopropyl acetate, the production of methyl isopropyl ether depends on the presence of isopropoxy radicals which can decompose more rapidly at the higher temperature by reactions (10) or (11),   leading to a lower effective concentration of such radicals for ether production.

The effect of temperature on the yield of polymer from isopropenyl acetate is of about the same order of magnitude as the effect on the yield of other products. If the termination of the polymerizing chain was caused by a high-activation-energy step for the addition of subsequent isopropenyl acetate molecules, one would expect a 50° change in temperature to dramatically increase the polymer yield, as there should then be a much smaller effect on the termination step than on the propagation steps. For comparison, a simple experiment in the radiochemical polymerization of styrene monomer showed a factor-of-10 increase in polymer yield for a temperature change from 25° to 80°, with a corresponding increase in the molecular weight of the polystyrene produced. Thus, it must be concluded that the polymerization of isopropenyl acetate is not terminated by a high-activation-energy step for addition of subsequent monomer molecules.

Comparison with Mass Spectral Patterns.

The mass spectrometer ionization patterns of these two esters, shown in Table V, are consistent with the previous conclusion that the alkoxy-acetyl bond is most susceptible to rupture. In each case the largest peak is at mass 43. Certainly the composition of this mass is CH_3CO^+ in the mass spectrum of isopropenyl acetate, and probably mostly CH_3CO^+ in the mass spectrum of isopropyl acetate, since the peaks at masses 39 and 38 are relatively small, indicating large yields of isopropyl ions to be improbable.

In the mass spectrum of isopropyl acetate, two rearrangement peaks are significant. Mass 61, which has the empirical formula $C_2H_5O_2$ from the distribution of isotope peaks at masses 62 and 63, must have the structure $CH_3COOH_2^+$. A precedent for this structure is the peak at mass 33 in the mass spectrum of some alcohols,[10]

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(10) Friedel, R. A., Shultz, J. L., and Sharkey, A. G., Jr., Anal. Chem. 28, 926 (1956).

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which has the structure $CH_3OH_2^+$. The formation of the ion $CH_3COOH_2^+$ also leads to the formation of the allyl radical.

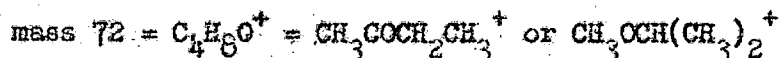$$M_1 + e^- \longrightarrow CH_3COOH_2^+ + C_3H_5 \cdot + 2e^- \tag{27}$$
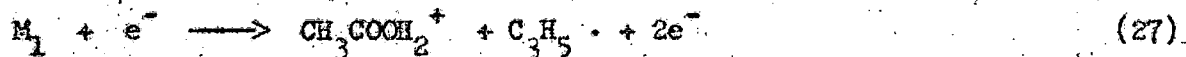
The ion, $CH_3COOH_2^+$, will, on neutralization, form acetic acid and a high-energy hydrogen atom. The allyl radical, on reaction with another radical, can yield either C_3H_4 or a higher alkene.

$$C_3H_5 \cdot + R \cdot \longrightarrow C_3H_4 + RH \tag{28}$$
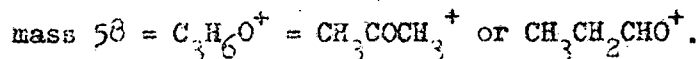
$$\longrightarrow RC_3H_5 \tag{29}$$
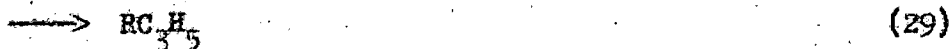
These reactions present possible mechanisms for the formation of the minor products C_3H_4 and isobutene in isopropyl acetate irradiations.
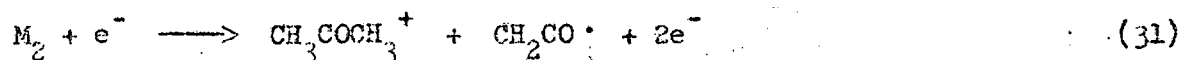
By a similar isotope-distribution argument, the ion at mass 45 is shown to have the empirical composition $C_2H_5O^+$, and on charge neutralization this probably leads to acetaldehyde and a high-energy hydrogen atom. It is curious that the fragmentation of the isopropyl acetate molecule ion on either side of the oxygen atom leads to the effective transfer of a hydrogen molecule from the isopropyl group to the oxygenated fragment which also carries the charge.

The mass spectrometer ionization pattern of isopropenyl acetate shows two molecular fragments as ions at masses 58 and 72. The evidence on composition from isotopic distribution of the next two higher masses is not so clear-cut in these two cases, but the data are best fitted by the following empirical compositions and related structures:

$$\text{mass } 72 = C_4H_8O^+ = CH_3COCH_2CH_3^+ \text{ or } CH_3OCH(CH_3)_2^+$$

mass $58 = C_3H_6O^+ = CH_3COCH_3^+$ or $CH_3CH_2CHO^+$.

From the evidence of the radiolysis experiments, the first structure is to be preferred in both cases, since methyl ethyl ketone and acetone are both products of the radiolysis of isopropenyl acetate. The following equations describe the process.

$$M_2 + e^- \longrightarrow CH_3COCH_2CH_3^+ + CO + 2e^- \qquad (30)$$

$$M_2 + e^- \longrightarrow CH_3COCH_3^+ + CH_2CO \cdot + 2e^- \qquad (31)$$
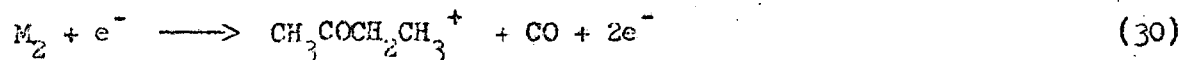
Methyl ethyl ketone is formed in the mass spectrometer by a first-order process, because the pattern does not change with pressure. It is, therefore, a case of a true methyl rearrangement in a unimolecular process. The authors do not wish to postulate a mechanism at this time, except to note that, structurally, conditions are favorable for the odd electron to bridge between the methylene group and the methyl group of the acetate. This might thus lead to the transfer of a hydrogen from the methyl group to the methylene group, leading to acetone ion, or to the transfer of the entire methyl group from the acetate to the methylene group, in turn leading to methyl ethyl ketone ion. The mechanism would imply the formation of ketene as a co-product of acetone production by this process. No ketene was observed as a radiolysis product.

In conclusion, it may be stated that the ions produced from these two compounds in the mass spectrometer are consistent with the products observed in the radiolysis of these same compounds with high-energy helium ions.

Table I

Properties of Irradiated Compounds

	Isopropyl Acetate		Isopropenyl Acetate	
	Found	Lit.	Found	Lit.[a]
d_4^{25}	0.8647	---	0.9151	0.91643
d 20/4 (calc.)	0.8746	0.8718[b]	---	---
n_D^{25}	1.3747	---	1.3984	1.39859
n_D^{20} (calc.)	1.3770	1.3773[b]	---	---
F.P.	$-74.8 \pm 0.5^\circ$	-73.4^c	$-86.0 \pm 0.5^\circ$	-85.37°
B.P.	88.4° (760mm)	-88.2^b	97.4°(760mm)	97.4

a. R. R. Dreisbach, "Physical Properties of Chemical Substances," Dow Chemical
   Co., Midland, Mich., Serial No. 21.12, Jan. 18, 1953.

b. A. Vogel, J. Chem. Soc., 624 (1948).

c. "Technique of Organic Chemistry," A Weissberger, Editor, Interscience Publishers
   Inc., New York, Vol. VII, "Organic Solvents" J. A. Reddick and E. E. Toops, 2nd
   Edition, 1955, p. 161.

Table II

Products from the Radiolysis of Isopropyl Acetate and Isopropenyl Acetate at 25°.

	Isopropenyl acetate		Isopropyl acetate			
Vol. (ml)	128.5	116.3	125.2	118.6	98.8	79.0
Energy Input ev/ml x 10^{-20}	1.126	4.009	1.112	4.12	13.81	58.6
Product	Yield of product in molecules/100 ev.					
Hydrogen	0.255	0.258	0.86	0.85	0.84	0.79
Carbon monoxide	1.61	1.72	1.17	1.19	1.18	1.17
Methane	0.218	0.239	0.94	0.94	0.93	0.93
Acetylene	0.022	0.024	0.028	0.027	0.031	0.023
Ethylene	0.035	0.035	0.021	0.020	0.022	0.021
Ethane	0.152	0.163	0.57	0.59	0.60	0.58
Propyne[a]	0.137	0.140	0.017	0.022	0.025	0.020
Propadiene[a]	0.101	0.107				
Propylene	0.036	0.038	0.77	0.77	0.71	0.67
Propane	----	----	0.152	0.139	0.147	0.139
Butadiene[b]	~0.0016	~0.0012	~0.002	~0.004	~0.004	~0.002
Isobutene	0.033	0.034	0.016	0.023	0.024	0.024
Isobutane	----	----	0.25	0.22	0.25	0.23
Neopentane[b]	----	----	~0.001	~0.003	~0.021	~0.011
Diisopropyl	----	----	0.033	0.023	0.023	>0.010
Carbon dioxide	0.34	0.35	0.75	0.79	0.80	0.84
Acetaldehyde	0.33	0.34	1.67	1.40	1.28	~0.78
Acetone	2.88	1.86	0.65	0.53	0.30	~0.22
Methyl isopropyl ether	----	----	0.26	0.19	0.17	>0.06
Isopropenyl acetate	----	----		$0.1 {}^{+.1}_{-.05}$	0.1 ± .05	0.1 ± .05
Methyl-ethyl ketone						
"Polymer"[c]	10.0	9.0	0.34	0.33	0.61	0.66
M.W. "Polymer"[c]	348 ± 4	358 ± 4	----	----	----	262 ± 2
Acetic acid	(d)	(d)	0.9	0.8	0.8	0.6

a. Propadiene - Propyne ratio known only approximately because of similarity of mass spectrometer patterns. Total is accurate for total C_3H_4. No split possible in Isopropyl Acetate samples.

b. Identification not certain.

c. "Polymer" includes all high-boiling products. Yield calculated assuming composition to be the same as original material and is the number of molecules of irradiated liquid/100 ev. reacting to give the observed-weight polymer. M/W. "Polymer" by freezing point lowering in benzene.

d. No acid seen by neutralization equivalent of irradiated material. Results show less acid than starting material. Gas chromatograms shows acetic and to be formed but no G value could be calculated.

e. Not determined on this irradiation.

Table III

Comparison of Yields of Some Products from Isopropyl Acetate

and Isopropenyl Acetate at 25° and 80°

Compound	Isopropyl acetate			Isopropenyl acetate		
Temperature	25° [a]	80°		25°	80°	
Volume		137.1		113.6	140.1	
Energy Input ev/m/x 10^{-20}	~2.0	2.10		2.45	2.46	
Product	Yield, G		% Change[b]	Yield, G		% Change[b]
H_2	0.85	0.99	+16%	0.26	0.29	11%
CO	1.18	1.52	+29%	1.65	2.33	+50%
CH_4	0.94	1.12	+19%	0.23	0.26	+13%
C_2H_2	0.027	0.034	+25%	.023	0.034	+50%
C_2H_6	0.58	0.77	+33%	.155	0.24	+50%
C_3H_4	0.020	0.034	+70%	.24	0.29	+20%
C_3H_6	0.77	0.87	+13%	.037	0.041	+10%
C_3H_8	0.145	0.17	+18%	---	---	---
$1\text{-}C_4H_8$	0.020	0.020	---	0.034	0.040	+18%
$1\text{-}C_4H_{10}$	0.23	0.38	+65%	---	---	---
CO_2	0.77	0.95	+23%	0.34	0.43	+26%
CH_3CHO	1.50	1.68	+12%	0.33	0.23	-30%
Acetone	0.60	0.61	±1%	~2.5	~1.4	-45%
Methyl Isopropyl ether	0.24	0.19	-20%	---	---	---
Polymer	0.34	---	---	~10	~13	+30~

a. Data interpolated from Table I.

b. % Change $= \dfrac{(G_{80^\circ} - G_{25^\circ})}{G_{25^\circ}} \times 100.$

Table IV

Yields of Hydrogen and Corresponding Hydrocarbon Products from
the Radiolysis of Isopropyl Acetate and Isopropenyl Acetate
Normalized to a Methane Yield of Unity

Isopropyl Acetate		Isopropenyl Acetate	
Product	Relative Yield	Product	Relative Yield
CH_4	1.0	CH_4	1.0
H_2	0.85	H_2	1.17
C_2H_6	0.61	C_2H_6	0.70
C_3H_6	0.82	C_3H_4	1.10
C_3H_8	0.16	C_3H_6	0.16
$1-C_4H_{10}$	0.30	$1-C_4H_8$	0.15

Table V

Principal Peaks in the Mass Spectra of Isopropyl Acetate
and Isopropenyl Acetate

m/q	Pattern Isopropyl Acetate	Type Peak[a]	Pattern Isopropenyl Acetate	Type Peak[a]
14	3.99		6.04	
15	16.91		16.55	
27	9.87		6.42	
28	1.90		2.04	
29	3.42		3.79	
31	1.70	R	0.60	R
38	1.06		2.30	
39	6.30		9.38	
41	11.41		10.03	
42	7.98		7.13	
43	<u>100</u>		<u>100</u>	
44	3.02	i+R	2.40	i
45	6.81	R	0.12	i
57	0.21		2.38	
58	0.15		14.44	R
59	7.56		0.53	
60	0.59	i+R	0.09	
61	15.20	R	0.16	R
72	.02		5.99	R
73	.06		0.31	
85	---		0.02	
87	8.96		0.01	
100	---		4.47	P
102	0.17	P		

a. P = parent peak;   R = rearrangement peak;   i = isotope peak.