

[CONTRIBUTION FROM THE DIVISION OF CHEMISTRY, NATIONAL BUREAU OF STANDARDS, WASHINGTON, D. C.]

Intramolecular Rearrangements.¹ I. *sec*-Butyl Acetate and *sec*-Butyl FormateBY R. BORKOWSKI AND P. AUSLOOS²

RECEIVED AUGUST 22, 1960

The photolysis of *sec*-butyl acetate and *sec*-butyl formate in the vapor, liquid and solid phases has been studied at different temperatures and wave lengths. The distributions of the three butenes produced in the intramolecular rearrangements were found to vary with temperature in all three phases. In the vapor phase, a change in wave length has a pronounced effect on the ratios 1-butene/2-butenes and *cis*-2-butene/*trans*-2-butene. Both ratios increased with a decrease in wave length. In the liquid-phase photolysis, however, no dependence on wave length was observed, but a drastic change of the butene distribution occurred in the short temperature-range associated with the formation of the glassy state. A brief study of the pyrolysis of these compounds showed that, at temperatures greater than 300°, the temperature dependence of the butene distribution was essentially zero.

Introduction

It is now well established³ that ketones and aldehydes containing one or more hydrogen atoms in the γ -position dissociate photochemically into olefins and the corresponding ketones or aldehydes. This intramolecular rearrangement is generally considered to involve the formation of a six-membered ring. Indirect evidence has been obtained recently for the formation of the enol form of acetone in the photolysis of 2-hexanone.⁴

A number of carbonyl compounds which, on absorption of radiation, yield more than one type of olefin are now being investigated in this Laboratory. The type of olefin formed depends on which hydrogen atom is transferred to the carbonyl group. A study of the change in distribution of these olefins with temperature, wave length and phase may be expected to provide a better insight into the nature of these primary events.

Previous investigations on the pyrolysis⁵ and photolysis⁶ of esters have shown that esters containing a β -hydrogen atom in the alkoxy group may decompose, by an intramolecular rearrangement, into an olefin and the corresponding acid. This paper reports the effects of wave length, temperature and phase on the distribution of the butenes produced in the photolysis of *sec*-butyl acetate and *sec*-butyl formate. The results are compared with the distributions obtained in the pyrolysis of these compounds.

Experimental

Apparatus.—The gas phase was photolyzed in a quartz cell (10 cm. in length, 5 cm. in diameter) enclosed in a heavy aluminum furnace provided with double quartz windows. The temperature was automatically controlled within half a degree.

The liquid phase (and also the glassy state) was irradiated in a quartz cell (0.05 cm. in length, 4.5 cm. in diameter) provided with two outlets, one of which was sealed after filling and the other closed by a break seal. The cell was immersed in a Pyrex Dewar flask with double quartz windows. Water was used in a constant temperature bath for experiments conducted at temperatures from 0 to 85°, and cold isopentane was the refrigerant for those conducted at temperatures below 0°.

(1) This research was supported by a grant from the U. S. Public Health Service, Department of Health, Education, and Welfare.

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(3) For a review see: J. N. Pitts, Jr., *J. Chem. Educ.*, **34**, 112 (1957).

(4) R. Srinivasan, *THIS JOURNAL*, **81**, 5061 (1959).

(5) (a) R. B. Anderson and H. H. Rowley, *J. Chem. Phys.*, **47**, 454 (1943); (b) A. T. Blades, *Can. J. Chem.*, **32**, 366 (1954).

(6) (a) P. Ausloos, *ibid.*, **34**, 1709 (1956); (b) P. Ausloos, *ibid.*, **36**, 383 (1958); (c) P. Ausloos, *THIS JOURNAL*, **80**, 1310 (1958).

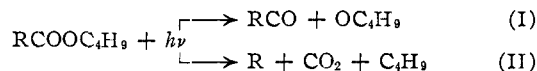
Hanovia S 100 lamps were used in all photochemical experiments. It was rather difficult to use monochromatic light at high intensities, because esters absorb appreciably at wave lengths less than 2350 Å. only. Corning filters 9-54 and 7-54, transmitting radiation at wave lengths greater than 2200 and 2300 Å., respectively, were used instead.

Analysis.—The analytical section of the vacuum system consisted of a sequence of traps, a modified Ward still and a Toepler pump. The non-condensable gases and the two-carbon and CO₂ fractions were usually discarded. In the liquid-phase experiments, these fractions were very small compared to the butene fraction. The butenes were removed at -110° and subsequently analyzed with a gas chromatograph. A Perkin-Elmer column "L" was used at 0°.

Conversions were about 1% in most experiments on the vapor phase and less than 0.1% for those on the liquid phase.

Results and Discussion

Besides the intramolecular rearrangements producing butenes, two dissociative processes also occur

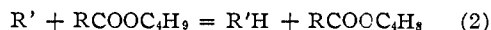


Primarily process II may also be written as a sequence of two steps^{6b} involving a COOC₄H₉ radical.

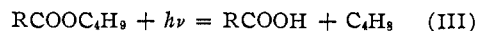
A butene may be produced in the disproportionation reaction



or be formed from the thermal decomposition of the RCOOC₄H₉ produced in the abstraction reaction



In order to prevent occurrence of reactions 1 and 2, we generally added oxygen to the vapor phase. Under these conditions, butenes were the only hydrocarbons detected among the products, and their formation can be ascribed only to primary process



Experimental data are given in Tables I and III. A comparison of the results for experiments 1 and 2 of Table I, as well as those for experiments 5 and 6 of Table III, shows that the rate of formation of the butenes and their distribution in the absence and presence of oxygen are not greatly different. This indicates that reactions 1 and 2 are not very important under these conditions. The results given in Table I also indicate that the rates of formation of the three butenes are, within experimental error, independent of the oxygen pressure.

TABLE I

VAPOR-PHASE PHOTOLYSIS OF *sec*-BUTYL ACETATE EFFECT OF OXYGEN

Oxygen, pressure, cm.	Yield of butenes, cc. (S.T.P.)/ min. $\times 10^4$	—Distribution of butenes, %—			
		1-butene	<i>trans</i> -2-butene	<i>cis</i> -2-butene	
0.1	4.1	29.8	47.6	22.6	
.25	4.25	30.4	47.5	22.2	
.60	3.9	29.7	48.3	22.0	
3.5	4.40	26.6	49.4	24.0	

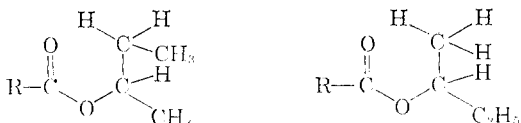
Recently, Brunet and Noyes⁷ reported similar results for the 2-hexanone-oxygen system. They concluded that, since oxygen does not inhibit the intramolecular rearrangement, the dissociating molecule is in an electronically excited, singlet state. This conclusion is based on the assumption that a molecule in the triplet state always reacts with oxygen.

TABLE II

VAPOR-PHASE PHOTOLYSIS OF *sec*-BUTYL ACETATE AND *sec*-BUTYL FORMATE EFFECT OF TEMPERATURE

Temp., °C.	Yield of butenes, cc. (S.T.P.)/ min. $\times 10^4$	—Distribution of butenes, %—			
		1-butene	<i>trans</i> -2-butene	<i>cis</i> -2-butene	<i>cis/trans</i>
<i>sec</i> -Butyl acetate					
43	4.75	30.4	47.4	22.2	0.47
123	4.04	32.3	44.0	23.7	.54
155	5.10	34.4	41.5	24.1	.58
<i>sec</i> -Butyl formate					
43	10.5	31.4	42.7	25.9	0.61
154	10.46	37.6	34.1	28.3	.83

The Effect of Wave Length and Temperature on the Photochemical Decomposition.—The intramolecular rearrangements in the pyrolyses and in the photolyses of esters containing β -hydrogen atoms may be expected to occur through formation of a six-membered ring as an intermediate. In the case of the *sec*-butyl esters, either a primary or a secondary β -hydrogen atom can be transferred to the carbonyl group



cis-2-butene and *trans*-2-butene will be formed if a secondary hydrogen atom is transferred, and 1-butene will be produced if a primary hydrogen atom is transferred. Because there are three primary and two secondary β -hydrogen atoms, a chance distribution corresponds to 60% of 1-butene and 40% of 2-butene.

Previous studies of pyrolysis⁵ have shown that a process involving the "split-out" of an olefin requires an activation energy of approximately 30 kcal. In the photochemical process, however, 125 to 140 kcal. is absorbed by the ester. This leaves an excess of 95 to 110 kcal., which must be distributed between the two fragments. Vibrational deactivation prior to the decomposition process may, of course, diminish this amount considerably.

(7) V. Brunet and W. A. Noyes, Jr., *Bull. soc. chim. (France)*, 121 (1958).

TABLE III

VAPOR-PHASE PHOTOLYSIS OF *sec*-BUTYL ACETATE AND *sec*-BUTYL FORMATE EFFECT OF WAVE LENGTH

Filter	Pressure oxygen, cm.	Yield butenes, cc. (S.T.P.)/ min. $\times 10^4$	—Distribution of butenes, %—			
			1-butene	<i>trans</i> -2-butene	<i>cis</i> -2-butene	<i>cis/trans</i>
<i>sec</i> -Butyl acetate						
None	..	60.5	43.0	36.0	21.0	0.58
None	0.2	58.2	37.0	40.7	22.3	.55
N.d. ^a	.2	5.7	37.1	41.2	21.7	.53
9-54	.2	4.25	30.4	47.4	22.2	.47
7-54	..	0.034	25.6	49.1	25.3	.51
7-54	.2	0.032	23.8	52.5	23.7	.45
<i>sec</i> -Butyl formate						
None	0.2	43.7	35.9	38.2	25.9	0.68
9-54	.2	10.5	31.4	42.7	25.9	.61
7-54	.2	00.18	25.1	47.6	27.3	.57

^a Neutral-density filter.

Vapor Phase.—The results given in Tables II and III indicate that an increase in temperature and a decrease in wave length cause an increase of the ratios 1-butene/2-butenes and *cis*-2-butene/*trans*-2-butene. These changes occur for both the formate and the acetate. The data of Table III indicate that, if the ester is in a very excited state, the butene distribution may eventually approach the chance distribution of 3:1:1.

The increase of the fraction of 1-butene with increase in energy is consistent with the fact that the bond strength of the primary hydrogen atom is greater than that of the secondary hydrogen atom. The increase of the ratio *cis/trans* with increase in temperature and decrease in wave length is probably related to the greater amount of energy removed by the butene fragment under these conditions. It is conceivable that an olefin excited electronically, or highly vibrationally, is produced and may surmount the activation energy-barrier for the *cis-trans* isomerization. We may predict that, the greater the excess energy taken up by the 2-butene, the closer will the ratio *cis/trans* approach a chance value near unity. The data show that the *cis/trans* ratio is consistently larger for the formate than for the acetate. In view of the smaller number of vibrational modes in formic acid as compared to the number in acetic acid, it may be expected that, under otherwise identical conditions, a larger fraction of the excess energy will be removed by the butenes produced in the photolysis of the formate.

Liquid Phase.—The results given in Table IV show that, at temperatures comparable with those at which the vapor-phase experiments were performed, the ratios 1-butene/2-butenes and *cis/trans* are much smaller for the liquid phase. In view of the dependence of these ratios on energy, as discussed in the preceding section, it seems reasonable to conclude that the dissociating molecule in the liquid phase is in a lower level of excitation than such a molecule in the vapor phase. The high rate of collision in the liquid phase may be expected to cause vibrational deactivation prior to the dissociative process. The results of experiments 3 and 4 of Table IV indicate that, in contrast to those for the vapor phase, a change in wave length has no significant effect on the distribution of the butenes.

It may thus be concluded that, no matter how highly excited the ester molecule is initially, collisional deactivation will always result in dissociation from the same low-lying level of energy. This conclusion is consistent with the fact that⁸ the absolute quantum yield of the fluorescence of a large number of organic compounds in solution is independent of the exciting wave length. According to Weber and Teale,^{8b} this fact is readily explained by assuming that the time required for vibrational deactivation to the ground-state of fluorescence is small compared to the natural radiative lifetime of this state.

TABLE IV
PHOTOLYSIS OF *sec*-BUTYL ACETATE IN THE LIQUID AND SOLID PHASES

Temp., °C.	Filter	Yield of butenes cc. (S.T.P.)/ min. × 10 ⁴	Distribution of butenes, %			
			1- butene	<i>trans</i> -2- butene	<i>cis</i> -2- butene	% <i>cis</i> / <i>trans</i>
83.1	9-54	11.9	17.2	59.2	23.6	0.40
33	9-54	10.0	14.5	62.9	22.6	.36
2	9-54	7.5	12.9	65.8	21.3	.32
2	None	20.3	12.8	65.6	21.6	.33
-28.2	None	19.8	12.2	66.6	21.2	.32
-53.0	None	16.5	13.0	67.5	19.4	.29
-80.0	None	17.9	12.5	69.5	17.9	.26
-98.4	None	19.1	15.2	66.0	18.8	.28
-117	None	19.5	22.2	59.8	18.0	.30
-126.5	None	18.7	25.9	53.5	20.6	.38
-137	None	10.3	43.1	39.2	17.7	.45
-150	None	8.8	43.0	40.7	16.3	.40
-156	None	8.6	46.8	37.8	15.4	.40
-156 ^a	None	8.7	42.8	42.9	14.3	.33
-158 ^b	None	8.2	41.5	44.3	14.2	.32
-158 ^c	None	8.9	42.0	43.0	15.0	.35
-195	None	3.50	59.1	26.6	14.3	.54

^a These experiments were performed in solution consisting of 7 vol. of 2-propanol + 3 vol. of ester. ^b These experiments were performed in solution consisting of 7 vol. of methanol + 3 vol. of ester. ^c These experiments were performed in solution consisting of 7 vol. of 1-propanol + 3 vol. of ester.

Although, in the photolysis of the liquid phase, the data show no dependence on wave length, those in Table IV indicate that there is a dependence on temperature. From -28 to +83°, the distribution of butenes undergoes a variation with temperature similar to that observed in the photolysis of the vapor phase. Hence, it may be concluded that the effect of wave length and temperature must be considered independently. This effect is understandable when we reflect that, initially, the photon energy is localized in the carbonyl group, whereas the thermal energy is distributed among all degrees of vibrational freedom. In the vapor phase, the effect of temperature may be expected to be less pronounced at shorter wave lengths. A more detailed comparison between the temperature effects for the liquid and the vapor phases will be given in a later publication.

At temperature below -80°, in contrast with the effect noted above, the ratio 1-butene/2-butenes increases slightly from -80 to -126°, and, at about -137°, increases markedly with a decrease

(8) (a) B. S. Neporent, *Zhur. Fiz. Khim.*, **21**, 1111 (1947); (b) C. Weber and F. W. J. Teale, *Trans. Faraday Soc.*, **54**, 640 (1958).

in temperature. The increase corresponds to a decrease in the total yield of butenes. Little change occurs between -137 and -156°. Solvents have practically no effect on the ratio 1-butene/2-butenes, although the ratio *cis/trans* may have decreased. At -195°, there is a further increase in the percentage of 1-butene. The presence of cracks in the glassy ester at this temperature may be partly responsible (because of an increase in light reflection) for the decrease in the total amount of butenes.

Although no obvious interpretation can be given for these observations, the sudden change in the distribution of butenes (which occurs near -135° and coincides with formation of the glassy ester) seems to imply hindered rotation about the O-C bond in the glass. The large percentage of 1-butene at the lower temperatures indicates that, in the glassy ester, the configurations in which primary and secondary hydrogen atoms are frozen in close proximity to the carbonyl group occur with about equal probability.

Pyrolysis of *sec*-Butyl Acetate.—The thermal decomposition of *sec*-butyl acetate was investigated very briefly in a static system at different pressures and temperatures. The results given in Table V indicate that, from 180 to 303°, a pronounced increase of the ratio 1-butene/2-butenes, occurs, but, from 303 to 430°, there is only a slight trend in the distribution of butenes. The results obtained by Froemsdorf, *et al.*,⁹ at 450° have been included in the same table. These authors pyrolyzed *sec*-butyl acetate by dropping the liquid ester into the top of a vertical tube packed with Pyrex helices. They noted that the distribution of butenes was practically independent of temperature. More recently, Blades undertook a careful investigation of the pyrolysis of *sec*-butyl acetate and *sec*-butyl formate in a toluene-carrier gas-system.¹⁰ The temperature interval was 360 to 537°. Within experimental error, he found no temperature dependence for either ester. The last row of Table V gives the average distribution of butenes.

TABLE V
PYROLYSIS OF *sec*-BUTYL ACETATE

Temp., °C.	Pressure esters, cm.	Distribution of butenes, %		
		1-butene	<i>trans</i> -2- butene	% <i>cis</i> -2- butene
180	1.85	15.0	39.8	45.2
202	1.85	16.4	39.7	43.9
270	2.00	27.4	35.6	37.2
303	1.35	52.6	29.6	17.8
353	1.30	53.5	29.8	16.7
388	0.35	54.2	29.2	16.6
407	1.30	54.3	29.2	16.5
430	2.35	55.4	28.8	15.9
450 ^a		57.0	28.0	15.0
360-537 ^b		53.0	29.2	17.8

^a See ref. 9. ^b See ref. 10.

It may thus be seen that the values obtained at high temperatures by the three different methods are in close agreement. The temperature depend-

(9) D. H. Froemsdorf, C. H. Collins, G. S. Hammond and C. H. DePuy, *THIS JOURNAL*, **81**, 643 (1959).

(10) A. T. Blades, unpublished results.

ence observed at low temperatures could be due to a heterogeneous decomposition of the ester on the wall. A more systematic investigation of the pyrolysis at low temperatures will be undertaken in the near future.

It has been suggested¹¹ that a photochemically induced rearrangement may be considered to be an

(11) J. Franck and H. Sponer, "Volume Commemorative V. Henri," Editions Desoer, Liège, Belgium, 1947, p. 169.

internal conversion involving a transition from one electronic state to a high level of vibration of a lower electronic state, thus producing a vibrationally excited molecule which may be expected to behave like a normal, thermally activated molecule. A comparison of the data from photolysis with those from pyrolysis indicates that there is no obvious analogy between the two modes of decomposition.

[CONTRIBUTION FROM THE DIVISION OF CHEMISTRY, NATIONAL BUREAU OF STANDARDS, WASHINGTON, D. C.]

The Effect of Solvents on the γ -Ray Radiolysis of Methyl Acetate and Acetone

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RECEIVED AUGUST 22, 1960

The effect of cyclohexane and benzene on the radiolysis of $\text{CH}_3\text{COOCH}_3$, $\text{CH}_3\text{COOCD}_3$, and mixtures of $\text{CH}_3\text{COCH}_2\text{-CD}_2\text{COCD}_3$ has been investigated at 17° . In the absence of scavengers, cyclohexane markedly reduces the yield of CO, whereas, in the presence of scavengers, it produces no effect. Benzene inhibits the decomposition of methyl acetate and acetone. Hydrogen is mostly formed in processes involving "hot" hydrogen atoms. The effect of the solvents on the yields of ethanes and some of the methanes indicates the importance of cage and intercage recombinations and disproportionations of the radicals in the γ -ray track. The radiolysis of a $\text{CH}_3\text{COCH}_2\text{-CD}_2\text{COCD}_3$ mixture at -195° is discussed briefly.

Introduction

The liquid-phase radiolysis of acetone¹ and methyl acetate^{2,3} has been investigated recently. The present paper reports the results of studies of the effect on the radiolytic decomposition of these compounds of varied amounts of benzene and cyclohexane. The studies were designed to reveal more detailed information on: (a) the reactions occurring in the γ -ray track, (b) the formation of the hydrogen molecule and (c) the scavenging action of carbon monoxide.

Experimental

Materials.—The compounds $\text{CH}_3\text{COOCD}_3$ and $\text{CD}_2\text{-COCD}_3$ were obtained from Merck and Company. They were purified by a trap-to-trap distillation at -80° and, subsequently, by distillation into the storage bulb from a trap at -40° . Mass-spectrometric analysis showed that the per cent. of deuterium in the deuterated acetone was 99.5 atom % of D and the methyl acetate to be 98.6% $\text{C}_2\text{H}_5\text{D}_2\text{O}_2$. From the cracking pattern, it was deduced that only the methoxy group was fully deuterated.

"Spectrograde" CH_3COCH_3 , C_6H_6 and C_6H_{12} were obtained from Eastman Kodak Company and used without further purification. All compounds were thoroughly degassed.

2,2-Diphenyl-1-picrylhydrazyl (DPPH) was obtained from Aldrich Chemical Company and was kept under vacuum until it was introduced into the cell.

Irradiations.—The liquids were irradiated in sample tubes made of Pyrex tubing, which were 15 cm. long and had an internal diameter of 0.35 to 0.8 cm. Each cell was provided with two outlets; one was sealed after filling and the other was closed by a break seal. The cells were filled by expanding each compound from its storage bulb into a one-liter bulb provided with a mercury manometer. After recording the pressure, the material was condensed into the reaction cell at -80° . The amount of methyl acetate or acetone introduced into the sample tube was 1 cc. and different amounts of cyclohexane or benzene subsequently were condensed into the cell. The diameter of the cell was adjusted in such a way that the liquid level was constant to within 3 mm. This procedure was adopted in order to insure a constant dose rate and to keep the methyl acetate or acetone conversion approximately constant without greatly

affecting the amount of products formed. The 2000-Curie source at the National Bureau of Standards was used in this investigation. It consists of twelve cobalt-60 sticks (19 cm. high, 1 cm. thick) arranged in a circular pattern (9 cm. i.d.) at the bottom of a water pool.

Usually, six samples were arranged in a reproducible, symmetrical pattern inside a cylindrical metal container. The container was sealed and then lowered into the center of the pool. The experiment at -195° was performed by immersing the sample in a narrow Dewar flask containing liquid nitrogen and placing the Dewar in the container.

The rates of absorption of energy were determined from the concentrations of ferric ion formed by irradiating 1 cc. of ferrous sulfate solutions. Assuming that $G(\text{Fe}^{+++}) = 15.45$, the rate of energy absorption was calculated to be 4×10^{17} ev./cc./min. In order to make the discussion easier to follow, the data given in Tables I, II and III are expressed in molecules/cc./min. multiplied by the ratio $(V_A + V_S)/V_A$. In this ratio, V_A is the volume of methyl acetate or acetone, and V_S is the volume of solvent. Both volumes are measured at STP. If required, the G values can easily be calculated from the dose rate given above.

TABLE I
RADIOLYSIS OF CYCLOHEXANE- $\text{CH}_3\text{COOCH}_3$ MIXTURES AT 17°

Concn. cyclohexane, mole %	Concn. scavenger, $10^{-3} M$	Time, min.	Rate $\times (V_A + V_S)/V_A \times 10^{-14}$, molec./cc./min.			
			H_2	CH_4	C_2H_6	CO
..	..	110	3.37	7.38	1.75	6.82
..	..	365	3.83	7.42	1.58	5.83
..	I_2	110	2.67	2.73	1.14	6.82
16.2	..	365	7.80	7.95	1.47	4.54
31.0	..	365	13.40	9.05	1.66	2.38
31.0	..	110	12.50	9.15	1.65	4.75
31.0	I_2	360	8.00	2.85	0.95	6.75
46.0	..	110	16.80	9.75	1.62	3.80

Analysis.—The analytical procedure was essentially the same as that described previously.^{1,3} Hydrogen, methane and carbon monoxide were distilled out at -195° , the C_2 fraction at -175° and the CO_2 fraction at -150° . All three fractions were analyzed with the mass spectrometer. Reference samples of CH_3CD_3 and C_2D_6 (obtained from Merck and Company) were analyzed in order to obtain reliable cracking patterns. The distribution of the methanes was calculated from cracking patterns reported in the literature.⁴

(1) P. Ausloos and J. Paulson, *THIS JOURNAL*, **80**, 5117 (1958).

(2) P. Ausloos and C. M. Trumbore, *ibid.*, **81**, 3866 (1959).

(3) R. W. Hummel, *Trans. Faraday Soc.*, **56**, 234 (1960).

(4) F. L. Mohler, V. H. Dibeler and E. Quinn, *J. Research Natl. Bureau Standards*, **61**, 171 (1958).