[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY, UNIVERSITY OF CHICAGO]

REACTIONS OF ATOMS AND FREE RADICALS IN SOLUTION. XXVII. THE DECOMPOSITION OF DIACETYL PEROXIDE IN ALCOHOLS

M. S. KHARASCH, J. L. ROWE, AND W. H. URRY

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INTRODUCTION

Dimers with structural units linked from *alpha* carbon atom to *alpha* carbon atom are obtained when diacetyl peroxide reacts with organic substances containing hydrogen atoms attached to carbon atoms *alpha* to various activating groups. When aliphatic acids (1, 2), esters (2, 3), nitriles (4), ketones (5), or alkylbenzenes (6) are used, the respective products are substituted succinic acids, succinic esters, 1,2-dinitriles, 1,4-diketones, and bibenzyls. For these reactions, a three-step mechanism featuring free radical intermediates is proposed. The three steps are: (a) the diacetyl peroxide decomposes to give free radical fragments, (b) these fragments (free methyl radicals) attack the solvent to yield methane and a free radical derived from the solvent, (c) two of these latter radicals unite to give the dimer.

The present investigation shows, on the other hand, that diacetyl peroxide reacts with primary and secondary alcohols to give aldehydes and ketones. This work was completed prior to the appearance of a paper by Bartlett and Nozaki (7) on the kinetics of the decomposition of benzoyl peroxide in alcohols. In that kinetic study no reaction products were isolated. Consequently the results obtained are insufficient for the construction of a reaction mechanism. It should be said, however, that the results here reported support Bartlett and Nozaki's postulate that the free radical attacks the hydrogen atom in the α-position of the alcohol. They do not support the idea that the free radical attacks the hydrogen atom of the (OH) group.

The decomposition of diacetyl peroxide in alcohols. Diacetyl peroxide has been decomposed in two primary alcohols, *n*-butyl and isobutyl; two secondary alcohols, isopropyl and *sec*-butyl; and one tertiary alcohol, *tert*-butyl. Quantitative results of these experiments are summarized in Tables I, II, and III.

The reactions of diacetyl peroxide with deuterium-labeled alcohols. Decomposition of diacetyl peroxide (16.9 g., 0.143 mole) in isopropyl alcohol (26.1 g., 0.435 mole; containing 40.9 mole-% of *O*-deuteroisopropyl alcohol) yielded methane which when burned gave water with only the usual proportion of deuterium oxide. Similarly, ordinary water was obtained by burning the methane formed in the reaction between diacetyl peroxide and *tert*-butyl alcohol containing 7.43 mole-% of *O*-deutero-*tert*-butyl alcohol.

On the other hand, when diacetyl peroxide was decomposed in isopropanol containing some 2-deuteroisopropyl alcohol ($CH_3CDOHCH_3$) a mixture of methane and deuteromethane (8) was obtained. Assuming that only the 2-hydrogen (or deuterium) atom of the alcohol is removed to form the methane, the rela-

TABLE I

The Decomposition of Diacetyl Peroxide in Isopropyl and *sec*-Butyl Alcohols[e]

PRODUCTS	YIELDS OF PRODUCTS (MOLES/MOLE OF DIACETYL PEROXIDE USED) IN	
	Isopropyl alcohol	*sec*-Butyl alcohol
Methane	1.05	1.01
Carbon dioxide	1.05	1.01
Ketone	0.888[a]	0.754[b]
Methyl acetate	.015	.028
Acetate esters of solvents	.330[c]	.446[d]
Acetic acid	.545	.411
Residue	2.5 g.	9.0 g.

[a] Acetone. [b] Methyl ethyl ketone. [c] Isopropyl acetate. [d] *sec*-Butyl acetate. [e] One mole of diacetyl peroxide was decomposed in six moles of alcohol.

TABLE II

The Decomposition of Diacetyl Peroxide in *n*-Butyl and Isobutyl Alcohols[h]

PRODUCTS	YIELDS OF PRODUCTS (MOLES/MOLE OF DIACETYL PEROXIDE USED) IN	
	n-Butyl alcohol	Isobutyl alcohol
Methane	0.92	1.03
Carbon dioxide	1.10	1.28
Carbon monoxide	0.358	0.222
Propane and propene[a]	.358	.222
Aldehyde	.137[b]	.117[c]
Methyl acetate	.084	.117
Acetate esters of solvents	.657[d]	.558[e]
Butyrate esters of solvents	trace[f]	.021[g]
Butyric acid	.036	.030
Acetic acid	.012	.030
Residue	36.2 g.	28.9 g.

[a] Propane (90%) and propene (10%). [b] *n*-Butyraldehyde (0.209 mole if combined aldehyde in the residue is included). [c] Isobutyraldehyde (0.197 mole if combined aldehyde in the residue is included). [d] *n*-Butyl acetate. [e] Isobutyl acetate. [f] *n*-Butyl butyrate. [g] Isobutyl isobutyrate. [h] One mole of diacetyl peroxide was decomposed in six moles of alcohol.

TABLE III

The Decomposition of Diacetyl Peroxide in *tert*-Butyl Alcohol

PRODUCTS	YIELDS OF PRODUCTS (MOLES/MOLE OF DIACETYL PEROXIDE USED) IN *tert*-BUTYL ALCOHOL
Methane	1.01
Carbon dioxide	1.45
Acetone	0.028
Methyl acetate	.252
tert-Butyl acetate	.028
Acetic acid	.231
Residue	21.8 g.

tive ease of attack upon hydrogen and deuterium ($k_H/k_D = 6.3$) here observed corresponds closely with the results obtained in other studies.

DISCUSSION

The products and yields of the reactions of diacetyl peroxide with secondary alcohols (Table I) and with *O*-deutero- and 2-deutero-isopropyl alcohol are consistent with the following mechanism.

1. $(CH_3COO)_2 \rightarrow CH_3\cdot + CO_2 + CH_3CO_2\cdot$
2. $CH_3\cdot + CH_3CHOHCH_3 \rightarrow CH_4$[1] $+ HO(CH_3)_2C\cdot$ (I)
3. $I + (CH_3COO)_2 \rightarrow CH_3\cdot + CO_2 + HO(CH_3)_2COCOCH_3$ (II)
4. $2\ I \rightarrow CH_3COCH_3 + CH_3CHOHCH_3$
5. $II \rightarrow CH_3COCH_3 + CH_3COOH$
6. $II + CH_3CHOHCH_3 \rightarrow H_2O + CH_3COCH_3 + CH_3COOCH(CH_3)_2$
7. $CH_3COO\cdot (CH_3COO-)_2\ CH_3COOCH_3 + CO_2 + CH_3COO\cdot$ (or $CH_3\cdot + CO_2$)

The proposed reaction mechanism has the familiar characteristics of a free radical chain reaction: initiation (reaction 1), propagation (reactions 2 and 3), and termination (reaction 4). Experiments with the deuterium-labeled alcohols show that free methyl radicals attack isopropyl alcohol as shown in reaction 2. In the reaction with 2-deuteroisopropyl alcohol the concentration of monodeuteromethane in the product was that which would be expected if only the 2-hydrogen is removed, reaction 2. In experiments performed with 40.9 mole-% O-deuteroisopropyl alcohol only ordinary methane was obtained.[2] The result shows that in the reaction in question, the hydrogen atom in the hydroxyl group of isopropanol is not attacked; hence reaction 2 must be favored. Furthermore, reaction 4 must be relatively unimportant and reaction 3 must predominate.

If the over-all reaction (for isopropanol and *sec*-butyl alcohol) follows only the mechanisms shown in reactions 1, 2, 3, 5, and 6, the (molar) yield of methane should equal the combined (molar) yields of acetic acid and acetate ester. Furthermore, the yield of ketone should be one-half the sum of the yields of methane, acetic acid, and acetate ester. The agreement between experiment and theory is on the whole very good. The two variations from the quantitative agreement (where only 75% of the products were accounted for) may be due to the ex-

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[1] The methane could also be formed as indicated below:

$$CH_3COO\cdot + CH_3CHOHCH_3 \rightarrow HO(CH_3)_2C\cdot + CH_4 + CO_2$$

On the basis of the data at hand it is difficult to assess the relative importance of the two mechanisms.

[2] These experiments prove conclusively that no free alkoxy radicals are formed in these reactions. Bartlett and Nozaki (7) [basing their argument on the claim of Gelissen and Hermans, *Ber.*, **58**, 765, 770 (1925) that *o*- and *p*-isobutoxybenzoic acids are formed in the reaction of benzoyl peroxide with isobutyl alcohol] have suggested that free alkoxy radicals are formed in the reaction. However, the claim of Gelissen and Hermans rests on questionable experimental evidence.

perimental difficulties, or to loss of radicals in the reaction which causes the formation of the polymeric materials ("Residue" in the Tables).

The reaction of diacetyl peroxide with primary alcohols is more complex, and (Table II) may be explained by assuming that aldehydes are first formed according to a mechanism analogous to the one shown for the formation of ketones. The aldehydes, since they are more reactive than the solvent alcohol, are then further attacked even though their concentrations in the reaction mixture are relatively low.

8. $CH_3CH_2CH_2CHO + CH_3\cdot$ (or $CH_3COO\cdot$) $\rightarrow CH_3CH_2CH_2(O{=}C\cdot) + CH_4$ (or CH_3COOH)

9. $CH_3CH_2CH_2(O{=}C\cdot) \rightarrow CH_3CH_2CH_2\cdot + CO$

10. $2\ CH_3CH_2CH_2\cdot \xrightarrow{20\%} CH_3CH_2CH_3 + CH_3CH{=}CH_2$[3]

11. $CH_3CH_2CH_2\cdot + CH_3CH_2CH_2CHO$ (or $CH_3CH_2CH_2CH_2OH$) $\rightarrow CH_3CH_2CH_3 + CH_3CH_2CH_2(O{=}C\cdot)$ (or $CH_3CH_2CH_2(HO)CH\cdot$)

The sum of the yields (in moles) of propane and propene has been found to be equal to the yield (in moles) of carbon monoxide (see Table II). This is the result required by the mechanism proposed.

The formation of acetate esters of the solvent (in the case of primary alcohols) probably proceeds in the manner indicated in equation 6. This equation suggests that the molar yield of the acetate esters should be the same as the molar yield of aldehyde and carbon monoxide. The discrepancy between the calculated and observed yields is due to further reactions of the butyraldehyde (9) resulting in the products called "Residue" in Table II. With secondary alcohols which give rise to ketones (Table I) that are only slightly attacked, the quantity of the "Residue" is very small.

The experiments with *tert*-butyl alcohol containing 7.43 mole-% of O-deutero-*tert*-butyl alcohol prove that only hydrogen atoms attached to a carbon atom are removed when this alcohol is attacked by free radicals. Furthermore, the products obtained in the reaction of diacetyl peroxide with *tert*-butyl alcohol, and the fact that the peroxide decomposes more slowly in tertiary than in primary or secondary alcohols, suggest that the reaction in question is not an induced-chain decomposition.

The derived free radicals formed in the reaction may react as follows:

1. $2\ HO(CH_3)_2CCH_2\cdot$ (III) $\rightarrow [HO(CH_3)_2CCH_2-]_2$

2. $HO(CH_3)_2CCH_2\cdot \rightarrow CH_3\cdot + CH_3COCH_3$

Acetone and the monoacetate of 1,1,4,4-tetramethylbutan-1,4-diol were isolated from the reaction mixture in question. It is interesting that the free radical (III) undergoes reaction 2, for this reaction is identical with the reaction

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[3] The propene could also arise from the loss of a hydrogen atom by the free propyl radical to some other free radical, or the peroxide molecule [*cf.* Kharasch and Buchi, *J. Am. Chem. Soc.*, **63**, 632 (1951).

of free *tert*-butoxy radicals postulated by Milas and Surgenor (10) to explain the products (methane and acetone) obtained in the high temperature decomposition of di-*tert*-butyl peroxide.

The high yield of methyl acetate obtained in the above reaction is unique. It demonstrates that in an unreactive solvent (*tert*-butyl alcohol), either the disproportionation of free acetoxy radicals, or the attack by free radicals upon the unreacted diacetyl peroxide becomes important.

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EXPERIMENTAL

General reaction procedure. A solution of diacetyl peroxide (0.5 mole) in the alcohol (1.5 mole) was introduced (over a period of four to five hours) beneath the surface of the same alcohol (1.5 mole) contained in a one-liter reaction flask immersed in an oil-bath held at 90°. A brisk evolution of gas was observed throughout the reaction. The gaseous products were passed first through the 50-cm. condenser attached to the reaction flask, then through a gas absorption train composed of two traps held at $-80°$, then through three large U-tubes (two containing soda-lime and the third containing Ascarite) and finally into a pneumatic trough.

The difference in the weight of the soda-lime and Ascarite tubes before and after the experiment indicated the amount of carbon dioxide formed.

Gas not condensed or absorbed was collected over water in the pneumatic trough. The yield of gaseous product was calculated from the volume (corrected) of gas collected. The molecular weight of the gas and the percentage of unsaturated compounds was determined according to the method of Kharasch, Lewis, and Reynolds (11). If the molecular weight of the gas corresponded to that of methane no further analysis was made. For gas mixtures, the carbon monoxide content was determined by absorption in ammoniacal cuprous chloride, using a Morehead apparatus (12).

Propane and propene were determined by liquefying the gas mixture in the vacuum line at the temperature of liquid nitrogen. The gases volatile at that temperature (methane and carbon monoxide) were pumped off. The molecular weight of the residual gas indicated that it was a mixture of propane and propene. The percentage of propene was then determined from the reduction in volume observed when the gas was passed through a bubble trap containing sulfuric acid.

The liquids condensed in the traps held at $-80°$ were allowed to warm to room temperature. Gases evolved during this operation were passed through an Ascarite tube to remove dissolved carbon dioxide. Gas not absorbed in this way was condensed in another trap held at $-80°$. This gas was analyzed as described above. Liquid remaining in the first trap was analyzed for its ester and aldehyde or ketone content.

The reaction mixture was distilled through a 12-plate column packed with single-turn glass helices. Because of the formation of azeotropes, it was not possible to separate the reaction mixture into its pure components. Various fractions were taken by distilling the liquid at atmospheric pressure until the boiling point of the solvent alcohol was reached. Then, the distillation was continued at a pressure of 100 mm., and further fractions were taken, until all products boiling below 100° at 100 mm. had been distilled. The residue was molecularly-distilled.

The weight and refractive index of each fraction were determined. The boiling point and refractive index of the fraction usually indicated what other substances were present along with the solvent alcohol, some of which was found in each fraction.

Fractions containing aldehydes and ketones were analyzed by quantitative precipitation of the 2,4-dinitrophenyl hydrazones, using the method of Ferrante and Bloom (13).

The various esters were determined by measuring the saponification equivalents of the fractions in which they occurred. Further, the amount of acid (acetic or butyric acids) was determined from the neutral equivalent of the fractions. For positive identification, *p*-bromophenacyl esters of the acids were prepared. Fractions containing only solvent alcohol were analyzed in the above manner as a measure of control.

The reaction of diacetyl peroxide with isopropyl alcohol. A solution of diacetyl peroxide (0.49 mole; 58 g.) in isopropyl alcohol (1.47 mole; 88.4 g.) was introduced below the surface of boiling isopropyl alcohol (1.47 mole; 88.4 g.), over a period of five hours. Quantitative details are given in Table I. The 2,4-dinitrophenyl hydrazone of acetone (m.p. 127–128°) was prepared from ketone-containing fractions.

The *p*-bromophenacyl ester of acetic acid (m.p. 85°) was obtained from acid- and ester-containing fractions. A small distillation residue (1.23 g.) was obtained. It gave no precipitate when treated with 2,4-dinitrophenyl hydrazine, and no pine splinter test for 1,4-diketones.

Reaction of diacetyl peroxide with sec-butyl alcohol. Diacetyl peroxide (55.2 g.; 0.467 mole) dissolved in *sec*-butyl alcohol (89.5 g.; mole 1.21) was dropped into boiling *sec*-butyl alcohol (118.5 g.; 1.60 mole) over a period of four hours. Yield data are given in Table I.

The 2,4-dinitrophenyl hydrazone of methyl ethyl ketone (m.p. 117°, 0.352 mole) was prepared from ketone-containing fractions. Higher-boiling, predominantly acid fractions gave the *p*-bromophenacyl ester of acetic acid (m.p. 84.5°).

A high-boiling residue (4.2 g.) failed to give tests for the presence of ketones or 1,4-diketones.

Reaction of diacetyl peroxide with n-butyl alcohol. A solution of diacetyl peroxide (59.6 g.; 0.503 mole) dissolved in *n*-butyl alcohol (117.7 g.; 1.58 mole) was dropped into *n*-butyl alcohol (104.7 g.; 1.42 mole) held at 100° over a period of five hours. Products and yields are recorded in Table II.

Gaseous product (17.58 liters at S.C.; 0.784 mole) not condensed at −80° or absorbed in soda-lime tubes was analyzed as outlined in the general procedure. It contained methane (58.9%; 0.461 mole; obtained by difference), propane (16.2%; 0.125 mole; M.W., 43), propene (1.8%; 0.013 mole), and carbon monoxide (23%; 0.180 mole; determined by absorption in a Morehead apparatus). The average molecular weight of this gas mixture was 24.0 (calc'd for gas of this composition, 24.2). An additional quantity of mixed propane and propene (1.8 g.; 0.04 mole; M.W., 42.3) was condensed in the −80° traps. This sample also contained 10% propene.

From early fractions obtained by distillation of this reaction mixture, the 2,4-dinitrophenyl hydrazone of butyraldehyde (0.069 mole; m.p. 123°) was obtained. A high-boiling fraction (b.p. 60–85° at 100 mm.) contained acetic acid and an ester. Attempts to prepare a pure *p*-bromophenacyl ester from a saponified portion of this fraction were not successful. After repeated crystallizations, the derivative melted over a range between the melting point of the *p*-bromophenacyl *n*-butyrate and *p*-bromophenacyl acetate. Since the residue was shown to contain *n*-butyric acid, this fraction probably contained a mixture of acetic acid and butyrate esters (possibly ethyl butyrate).

Early fractions in this distillation separated into two layers. The lower layer contained water (3.47 g.; 0.19 mole).

The residue remaining after distillation (16.7 g.) was molecularly-distilled. A record of the properties of fractions of the molecular distillate and of their experimental study are included in Table IV. The fractions obtained are obviously mixtures. Molecular weights were determined cryscopically in benzene. The weight in grams of substance containing one equivalent of hydroxyl (acetylation number) was determined by the method of Freed and Wynne (14).

Fractions a and b were combined and, a sample (0.4 g.) mixed with a solution of 2,4-dinitrophenyl hydrazine (0.8 g.) in ethanol (30 cc.) containing concentrated hydrochloric acid (4 cc.) was heated on the steam-bath for one-half hour. When this reaction mixture was cooled the 2,4-dinitrophenyl hydrazone of *n*-butyraldehyde separated (0.3 g., m.p.

117°). From this combined fraction *n*-butyl 3,5-dinitrobenzoate (m.p. 64°) was prepared by the method of Renfrow and Chaney (15). The molecular weight of the sample and the preparation of these two derivatives in good yield indicates that probably one of the components of this residue is di-*n*-butyl *n*-butyral.

Fraction c gave no 2,4-dinitrophenyl hydrazone. The low saponification equivalent of this fraction indicates the presence of a high-boiling ester, probably the trimeric ester obtained in the decomposition of diacetyl peroxide in *n*-butyraldehyde.

The reaction of diacetyl peroxide with isobutyl alcohol. As outlined in the general procedure, diacetyl peroxide (59.4 g.; 0.502 mole) dissolved in isobutyl alcohol (134.6 g.; 1.82 mole) was added over a period of four hours to isobutyl alcohol (87.4 g.; 1.18 mole) held at 100°. Quantitative details are given in Table II.

TABLE IV

ANALYSIS OF HIGH-BOILING RESIDUES

ALCOHOL	*n*-BUTYL	ISOBUTYL	*tert*-BUTYL
Weight of residue, g.	16.7	14.5	10.1
Weights of molecular-distillate fractions, g.	(a) 4.2	(a) 1.2	(a) 2.0
	(b) 7.0	(b) 4.1	(b) 0.2
	(c) 4.1	(c) 2.8	
		(d) 0.5	
Molecular weights of molecular-distillate fractions	(a) 239	(b) 218	(b) 170
	(b) 274	(c) 260	
Undistilled residue	1.3	3.0	8.2
Acetylation number	(b) 692	(b) 920	
	(e) 595	(e) 585	
Saponification equivalent	(b) 2500	(b) 780	(a) 267
	(c) 522	(b) 780	(b) 170
Per cent aldehyde or ketone	(b) 21.4[a]	(b) 41.5[b]	(a) 3.8
		(c) 17.1	
Carbon-hydrogen analysis, %	(b) H, 12.09	(b) H, 10.43	(a) H, 9.37
	C, 68.69	C, 65.88	C, 64.45
	(c) H, 10.84	(c) H, 10.46	
	C, 67.00	C, 66.23	

[a] Calculated from the yield of the 2,4-dinitrophenyl hydrazone of *n*-butyraldehyde.

[b] Calculated from the yield of the 2,4-dinitrophenyl hydrazone of isobutyraldehyde.

As in the previous experiment, water (3.4 g.) was isolated as one of the reaction products. Here also attempts to prepare a pure *p*-bromophenyl ester from the acetic acid fraction failed. The melting point of the derivative formed (71–75°) remained unchanged after three recrystallizations from ethanol (80%). The fraction propably contained both acetic and isobutyric acids.

The high-boiling residue (14.5 g.) was molecularly-distilled. Results of the study of fractions of this distillation are given in Table IV. Both the 2,4-dinitrophenyl hydrazone of isobutyraldehyde (m.p. 177°) and isobutyl 3,5-dinitrobenzoate (m.p. 86°) were obtained in good yield from all three fractions to suggest that one component of this residue is diisobutyl isobutyral. The presence of saponifiable material also indicates the presence of a trimeric ester analogous to that suspected in the *n*-butyl alcohol experiment.

The reaction of diacetyl peroxide with tert-butyl alcohol. Diacetyl peroxide (54.9 g., 0.464 mole) dissolved in *tert*-butyl alcohol (82.7 g., 1.12 mole) was dropped into boiling *tert*-butyl alcohol (123.3 g., 1.68 mole). This reaction was much slower than those of the other alcohols studied. The peroxide was added over a period of eight hours, and five hours more were required to complete the decomposition of the diacetyl peroxide. Products and yields are summarized in Table III.

The unabsorbed gas obtained in this reaction was found to be pure methane (M.W., 16.9). Distillation fractions taken before the boiling point of *tert*-butyl alcohol was reached contained acetone (0.013 mole; determined as the 2,4-dinitrophenyl hydrazone, m.p. 127°) and methyl acetate (7.7 g.; 0.104 mole; determined by saponification equivalent). *p*-Bromophenacyl acetate (m.p. 85°) was prepared from higher-boiling fractions.

The high-boiling residue (10.1 g.) contained only a small fraction (2.2 g.) which would distill at a high vacuum. Upon standing, crystals (0.2 g., m.p. 78–79° after recrystallization from acetic acid and water) formed in this fraction. This crystalline material was probably the monoacetate ester of 2,5-dimethylhexan-2,5-diol.

Anal. Calc'd for $C_{10}H_{20}O_3$, C, 65.49; H, 9.66; Sapon. Equiv., 188.
Found: C, 64.45; H, 9.37; Sapon. Equiv., 170.

The liquid remaining in this fraction had a saponification equivalent of 267 suggesting that it contained more acetate esters of the above diol. When this oil was hydrogenated using Adams' catalyst in acetic acid solution, only a small amount of hydrogen was taken up. This showed that only a small amount of ketonic or other unsaturated material was present. When a sample of this material (1 g.) was oxidized with sodium hypoiodite, however, iodoform (0.013 g.) was obtained. Also, succinic acid (0.005 g.) was isolated as its *p*-bromophenacyl ester (m.p. 211°) from the alkaline reaction mixture. This indicated the presence of a small amount of acetonyl acetone in this residue fraction.

This result suggests the possible composition of the undistillable residue (8.2 g.). When diacetyl peroxide is decomposed in acetonyl acetone (5), polymers of an average molecular weight five times that of acetonyl acetone are formed. The residue in this *tert*-butyl alcohol reaction may be formed by the attack of free methyl radicals upon acetone to yield acetonyl acetone followed by further attack upon the acetonyl acetone to give high polymers.

The reaction of diacetyl peroxide with O-deuteroisopropyl alcohol. Isopropyl alcohol (60 g., 1 mole) was mixed with deuterium oxide (14 g., 0.7 mole). After standing overnight, the mixture was treated with ignited calcium oxide (45 g.), and the isopropyl alcohol was recovered by distillation. Further drying of the alcohol was accomplished by distillation from magnesium isopropoxide (10 g.). The alcohol was analyzed for O-deuteroisopropyl alcohol by the method of Brown, Wilzbach, and Urry (16). A sample of the alcohol (5 g.) was treated with three successive portions of methylmagnesium iodide in di-*n*-butyl ether. The three samples of methane were burned in dry air, and the water obtained was analyzed for deuterium oxide concentration by the flotation-temperature method. The results showed the following concentrations of *O*-deuteroisopropyl alcohol: Sample 1, 41.9 mole-%; sample 2, 40.5 mole-%; and sample 3, 40.2 mole-%.

Diacetyl peroxide (16.9 g., 0.143 mole) was decomposed in this isopropyl alcohol (26.1 g., 0.435 mole). The temperature was held at the boiling point of the reaction mixture. Carbon dioxide (5.0 g., 0.13 mole) and methane (3.5 liters) were obtained. The methane was obtained in four successive samples, and each was analyzed as described above. The water samples obtained upon combustion gave the following analyses: First liter, 0.02 mole-% D_2O; second liter, 0.00 mole-% D_2O; third liter, 0.00 mole-% D_2O; and last sample (½ liter), 0.00 mole-% D_2O.

The reaction of diacetyl peroxide with O-deutero-tert-butyl alcohol. Diacetyl peroxide (15 g.) was decomposed in *tert*-butyl alcohol (40 g., 0.54 mole); prepared as described above, and found to contain 7.43 mole-% *O*-deutero-*tert*-butyl alcohol. The three liter samples of methane obtained gave the flotation temperature of ordinary water.

SUMMARY

1. The rate of decomposition (and the products formed) of diacetyl peroxide in primary and secondary alcohols, but not in *tert*-butyl alcohol, suggest an induced-chain reaction.

2. It has been established that free radicals do not attack the hydrogen atom of the (OH) group of alcohols, but instead remove a hydrogen atom attached to a carbon atom.

3. The products formed in the decomposition of diacetyl peroxide in isopropyl, *sec*-butyl, *n*-butyl, isobutyl, and *tert*-butyl alcohol have been identified. A mechanism to account for these products is suggested.

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REFERENCES

(1) KHARASCH AND GLADSTONE, *J. Am. Chem. Soc.*, **65**, 15 (1943).
(2) KHARASCH, JENSEN, AND URRY, *J. Org. Chem.*, **10**, 386 (1945).
(3) KHARASCH, McBAY, AND URRY, *J. Org. Chem.*, **10**, 394 (1945).
(4) KHARASCH, SMITH, AND URRY, unpublished work.
(5) KHARASCH, McBAY, AND URRY, *J. Am. Chem. Soc.*, **70**, 1269 (1948).
(6) KHARASCH, McBAY, AND URRY, *J. Org. Chem.*, **10**, 401 (1945).
(7) BARTLETT AND NOZAKI, *J. Am. Chem. Soc.*, **68**, 1686 (1946); **69**, 2299 (1947).
(8) URRY AND COLTON, unpublished work.
(9) KHARASCH, GRAHAM, AND URRY, unpublished work.
(10) MILAS AND SURGENOR, *J. Am. Chem. Soc.*, **68**, 205 (1946).
(11) KHARASCH, LEWIS, AND REYNOLDS, *J. Am. Chem. Soc.*, **65**, 493 (1943).
(12) *Gas Chemist's Handbook*, page 96.
(13) FERRANTE AND BLOOM, *Am. J. Pharm.*, **105**, 381 (1933).
(14) FREED AND WYNNE, *Ind. Eng. Chem., Anal. Ed.*, **8**, 278 (1936).
(15) RENFROW AND CHANEY, *J. Am. Chem. Soc.*, **68**, 150 (1946).
(16) BROWN, WILZBACH, AND URRY, *Can. J. Research*, **B27**, 398 (1949).