found to be consistent with a mechanism in which only the un-ionized malonamic acid undergoes decomposition.

MADISON, WISCONSIN RECEIVED APRIL 10, 1950

[A CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

The Decomposition of Benzoyl Peroxide in the Presence of Iodine. II. In Carbon Tetrachloride Solution[1,2]

BY GEORGE S. HAMMOND AND LOUIS M. SOFFER

The first paper in this series reported the results of a study, by product analysis and kinetics, of the decomposition of benzoyl peroxide in the presence of iodine in the aromatic solvents benzene and chlorobenzene.[3] The results were found to be understandable and compatible with earlier work with peroxides if it was assumed that benzoate radicals produced in the primary process react with iodine to give the unstable compound, benzoyl hypoiodite, which was rapidly destroyed in non-radical reactions with the aromatic solvents. The object of the present investigation was to extend the study to decomposition in carbon tetrachloride solution containing iodine. It was hoped to obtain further information concerning both the primary process and the chemistry of the reaction between iodine and the benzoate radical by working in a solvent which not only shows very different reactivity toward certain free radicals,[4] but would also be expected to be unreactive toward electrophilic attack by the postulated intermediate.

Boëseken and Gelissen[5] reported among the products of the decomposition of benzoyl peroxide in carbon tetrachloride, ω-trichloro-*p*-toluic acid, carbon dioxide, chlorobenzene, hexachloroethane and phosgene. Kharasch and Dannley[6] in their study of the thermal decomposition of di-α-naphthoyl peroxide in carbon tetrachloride isolated carbon dioxide, hexachloroethane and α-chloronaphthalene as primary reaction products. α-Naphthoic acid, naphthalene-1,4-dicarboxylic acid and 4′-carboxy-1′-naphthyl 1-naphthoate were found as products resulting from hydrolysis of the reaction mixture.

Perret and Perrot,[7] studying the decomposition in the same solvent in the presence of iodine and olefins, observed that relatively little carbon dioxide was evolved and obtained high yields of the corresponding diol dibenzoates. The isolation of 2-iodocyclohexyl benzoate from cyclohexene and the fact that this material reacted further to yield the corresponding dibenzoate suggested to these investigators that benzoyl hypoiodite was involved.

Experimental

Benzoyl peroxide was twice recrystallized by dissolving in chloroform and pouring the solution into methanol; assay, 99.5% minimum.[8]

Iodine, Baker and Adamson reagent grade, was used without further purification.

Carbon Tetrachloride, Baker and Adamson reagent grade, was dried over anhydrous sodium sulfate and redistilled.

Product Analysis. (A).—A solution of 10.0 g. of iodine (0.0394 mole), 10.0 g. of benzoyl peroxide (0.0413 mole) in 160 ml. of carbon tetrachloride was placed in a 250-ml. glass bomb, the contents swept with dry nitrogen, sealed, and immersed in a thermostat at 79.0 ± 0.05° for 36–48 hours or until virtually all the peroxide had decomposed. After opening, a small amount (5–10 mg.) of a fine, light-colored sediment was removed by decantation through glass wool. A 10-ml. sample was withdrawn. The remaining solution (141 ml.) was decolorized with a few ml. of concentrated aqueous sodium thiosulfate, and then fractionated to remove most of the carbon tetrachloride–water azeotrope (66°). The residue was extracted with small portions of 100 ml. of aqueous sodium bicarbonate. After concentration, acidification and recrystallization 0.27 g. of benzoic acid (m. p. 119°) was obtained (no depression with authentic sample). Ether extraction of aqueous mother liquors yielded a further 0.15 g., melting at 119°.

The insoluble fraction from the aqueous bicarbonate extraction was fractionated under close observation, assuring the constant presence of water until all the carbon tetrachloride had distilled, as shown by the sudden rise in temperature above 67°. The two layers in the flask were separated. The lower yellow, oily layer, A, was steam distilled until the distillate was clear (500 ml. of distillate collected). On standing overnight the mixture separated into two layers, water and iodobenzene. After separation and drying, 7.1 ml. of iodobenzene was obtained (micro b. p. 188°, n^{20}_D 1.618, m. p. of *p*-nitro derivative 171°). Layer B was found to contain a negligible amount of iodobenzene. The yellowish semi-solid residue from the steam distillation of A could not be crystallized. Saponification in the usual way followed by recrystallization yielded 0.15 g. of benzoic acid. The phenolic component was isolated as 2,4,6-tribromophenol (m. p. 92.5–93.5°, no depression with authentic sample). Acetylation of the latter yielded 2,4,6-tribromophenyl acetate (m. p. 82°). This substance showed a definite depression when mixed with 2,5-dibromo-4-iodophenyl acetate (m. p. 87°).

(B).—A solution of 5.0 g. of iodine (0.019 mole), 5.0 g. of benzoyl peroxide (0.021 mole), 2 ml. of water and 80 ml. of carbon tetrachloride was prepared and treated exactly as in run (A). The bomb was removed from the thermostat after 41 hours. There was no solid present. The remaining solution (81.5 ml.) was decolorized with aqueous thiosulfate. After fractionation, a mass of white

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(1) Presented before the Physical and Inorganic Division at the 117th Meeting of the American Chemical Society, Detroit, April, 1950.

(2) We gratefully acknowledge the financial support of this work by the Office of Naval Research.

(3) Hammond, THIS JOURNAL, **72**, 3737 (1950).

(4) Mayo, *ibid.*, **65**, 2324 (1943).

(5) Boëseken and Gelissen, *Rec. trav. chim.*, **43**, 869 (1924).

(6) Kharasch and Dannley, *J. Org. Chem.*, **10**, 406 (1945).

(7) Perret and Perrot, *Helv. Chim. Acta*, **28**, 558 (1945).

(8) Liebhafsky and Sharkey, THIS JOURNAL, **62**, 190 (1940).

TABLE I

MATERIAL BALANCE FOR DECOMPOSITION OF BENZOYL PEROXIDE IN PRESENCE OF IODINE IN CARBON TETRACHLORIDE SOLUTION (79°)

Material	Input Amount G.	Input Amount Mole		Output Amount G.	Output Amount Mole	% of initial input on absolute basis Phenyl	% of initial input on absolute basis Iodine
Benzoyl peroxide	10.0	0.041	Iodobenzene	13.9	0.068	82.5	86.5
			Benzoic acid	0.45	.0036	4.4	
			Phenyl benzoate	0.26	.0013	3.1	
Iodine	10.0	0.039	Iodine		.00495		12.6
					Total	90.0	99.1

crystals and yellow solid (later shown to be sulfur) remained. The two solids could be separated manually or by alkaline extraction. After purification the white crystals were identified as benzoic acid, m. p. 121.2°, no depression on admixture with authentic sample. The combined yield of the acid from the various mother liquors was almost 5 g., or nearly quantitative. No iodobenzene was found.

(C).—A control was prepared for (B), of identical composition, but with iodine absent. When the sample was withdrawn after 42 hours it was pale yellow in appearance and contained a small amount of white particles in suspension. (This material was later shown to be acidic, high melting and halogen-free.) An aliquot of the solution was withdrawn for peroxide assay; titration indicated the solution contained 0.25 g. of peroxide. As before, the exact nature of the oxidant is questionable. The remaining solution was extracted with aqueous bicarbonate. Acidification yielded 0.55 g. of white solid which began subliming at 210° and did not melt under 280°. Recrystallization yielded a material which did not sublime but melted at 285–290°. Addition of bromine water to the acid solution gave a light turbidity. This and a faint odor indicated the presence of a trace of phenol. Fractionation of the residual carbon tetrachloride solution in a 42-plate column yielded 2 ml. of chlorobenzene (b. p. 127.5–130°, $n^{21.5}$D 1.521, m. p. of *p*-nitro derivative 83°). A fall in temperature and considerable charring of the solid in the flask halted the fractionation. The residue yielded hexachloroethane, m. p. 186° (sealed tube), after recrystallization from alcohol–ether. No benzoic acid was found.

Kinetic Runs (Nos. 11–15).—Carbon tetrachloride solutions of varying relative concentrations of iodine and peroxide were prepared. Four-ml. aliquots were added to constricted test-tubes, which had been cleaned in the acid-bath, rinsed in turn with ammonia and distilled water and dried in the oven at 120–130°. The tubes were degassed while frozen at Dry Ice–acetone temperature, sealed and placed in a thermostat at 79.0 ± 0.05°. Samples were removed at intervals, rinsed into 250-ml. erlenmeyer flasks with thiophene-free benzene and analyzed successively for iodine and peroxide. Iodine was determined by reduction with 0.1 *N* aqueous sodium thiosulfate. The peroxide in the residual solution was reduced by the addition of 50–60 ml. of glacial acetic acid, 1 ml. of saturated aqueous potassium iodide and Dry Ice. The iodine produced was titrated using its own color as an indicator. This oxidation of iodide was slow and was best carried out by warming the flasks on a hot-plate during the course of the titration. It was essential to exclude air from the flask by the constant presence of an adequate amount of Dry Ice.[9]

(No. 18).—A series of samples was prepared, by individual weighings, of relative composition identical to that of Product Analysis (A). After the tubes were sealed these were treated as described above.

(No. 19).—Approximately 0.1 ml. of distilled water was added to each tube before the degassing procedure was carried out.

Discussion and Results

Product Analysis (A).—A semi-quantitative material balance for the decomposition is shown in Table I. The products represent a total of 90.0% of the initial phenyl (or benzoate) input and 99.1% of the initial iodine input. It should be noted that attack on the solvent, an important reaction in the absence of iodine, was completely inhibited by its presence.

The low yields of products in which the benzoate function remains intact is in striking contrast to the results obtained in aromatic solvents containing iodine. This would seem, at first, to be at variance with the view that benzoyl hypoiodite is formed as a common intermediate in both reactions. However, we should remember that it was necessary to assume that the intermediate lost carbon dioxide even in the presence of aromatic compounds if the concentration of iodine was low. This suggested that a decarboxylation reaction is an alternative to the attack on the aromatic nuclei. Since no such reaction is to be expected with carbon tetrachloride the high yield of carbon dioxide is not surprising. It is a well known fact that the reaction of the silver salts of carboxylic acids, which probably involves similar intermediates,[10] effects the degradation of the acid in this same manner.[11] It is perhaps noteworthy that the high yield of iodobenzene (82%) suggests that a useful preparative procedure for aryl iodides could be developed through the use of this reaction.

Kinetics.—A study of the kinetics of the reaction has shown that the peroxide decomposition is first order with respect to peroxide and is independent of the iodine concentration over the range studied (Table II). It is of interest that the unimolecular rate constant is considerably smaller than the value (0.092 hr.$^{-1}$) found in benzene.[3] Since it is felt that the decompositions in both instances were free of any significant amount of induced processes, this difference must be laid to intrinsic solvent effects on the "true" unimolecular rate constant.

Iodine "titers" are plotted against peroxide in ml. of equivalent thiosulfate in Fig. 1. The apparent relative rate of iodine uptake shows a curious behavior. During the early part of the runs the iodine titer either remained approximately constant (runs 11 and 14) or increased slightly (runs 12, 13, 15 and 18). After these initial periods, which vary in duration from

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(9) For discussion of procedure see ref. 3.

(10) Oldham and Ubbelohde, *J. Chem. Soc.*, 368 (1941).

(11) Kleinberg, *Chem. Revs.*, **40**, 381 (1947).

TABLE II

KINETICS OF BENZOYL PEROXIDE DECOMPOSITION IN IODINE AND CARBON TETRACHLORIDE AT 79.0°

Run	Initial peroxide (moles/liter × 10²)	Initial iodine (moles/liter × 10²)	k_1 in hr.⁻¹	dx/dP
11	6.82	5.75	0.061	1.13
12	2.64	4.05	.061	0.34
13	6.60	3.08	.061	.69
14[a]	4.63	6.62	.061	.69
15[b]	4.84	7.07	.069	.83
18[c]	25.8	24.6	.083	.93
19	5.33	5.02	.061	..

[a] The decomposition was interrupted after ninety minutes, the peroxide concentration restored to its original value, and the run continued as usual. [b] One ml. of iodobenzene was added initially per 100 ml. of solution. [c] The larger rate constant is probably the result of the heterogeneous system which exists in the early part of this run.

about thirty minutes to over two hours, the titration values begin to fall off and in the later stages of the runs there is a nearly linear relationship between peroxide and "iodine." Considerable difficulty was experienced in attempting to duplicate the results of the various runs until it was noticed that the amount of aqueous thiosulfate reduced in the iodine assays was appreciably smaller in samples which were allowed to stand for a time at room temperature. In runs, not reported in detail, in which the samples were all allowed to stand at room temperature for twenty-four hours or longer before the analyses were performed, the iodine titer was observed to decrease from the very first. On the other hand, no change occurred if samples were chilled to Dry Ice temperature immediately after removal from the bath.

These results indicate that some unstable intermediate capable of oxidizing thiosulfate was accumulating in solution during the early stages of the run. This intermediate must be some substance which decomposes to give iodobenzene, the principal reaction product. The decomposition of this substance must be characterized by rather low activation energy since the reaction proceeds at a measurable rate at both room temperature and 79°.

Reaction in the Presence of Water.—It seemed quite possible that benzoyl hypoiodite might fulfill the above mentioned requirements. Another characteristic of this type of compound is susceptibility to rapid hydrolysis.[10] The small amount of benzoic acid found among the reaction products could have arisen through the hydrolysis of the hypoiodite which remained in solution at the end of the experiment. When water was added to the reaction mixture at the beginning of the run a virtually quantitative yield of benzoic acid was obtained. In a control experiment in which water, but no iodine, was included in the reaction mixture no significant amount of benzoic acid was produced by chlorobenzene and hexachloroethane, the usual products of decomposition in carbon tetrachloride, were isolated from the reaction mixture.

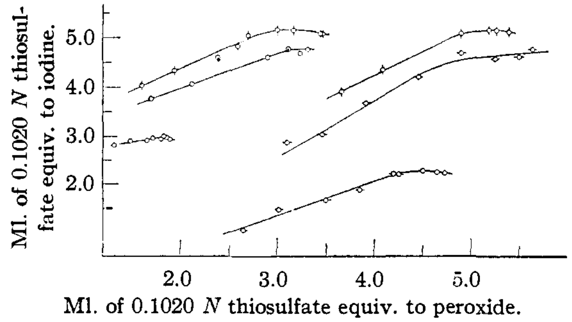

Fig. 1.—Kinetics of iodine consumption

Symbol	Run no.	Symbol	Run no.	Symbol	Run no.
-o-	11	-o-	13	⊙	15
○	12	⊙	14	ϕ	18[a]

[a] Titers plotted are one-half of actual values.

An additional control was obtained by following the rate of peroxide decomposition in the presence of both iodine and water. This was necessary because of the possibility that benzoic acid was produced in some reaction involving water, iodine and peroxide. For example, the small concentration of hydrogen iodide, formed by the hydrolysis of iodine, could conceivably have been sufficient to reduce the peroxide rapidly. The results of run 19 indicate that the decomposition is not accelerated. The "iodine titer" rose slightly in the initial part of the run and then decreased to approximately the initial value and remained constant. It is apparent that the other product of the reaction, presumably an oxy-acid of iodine, is not quantitatively reduced under the conditions of the analyses.

Mechanism.—The following sequence is postulated to be, in essence, the mechanism of the decomposition.

$$(C_6H_5COO)_2 \xrightarrow{k_1} 2C_6H_5COO\cdot \qquad (1)$$

$$C_6H_5COO\cdot + I_2 \xrightarrow{k_2} C_6H_5COOI + I\cdot \qquad (2)$$

$$C_6H_5COOI \xrightarrow{k_3} C_6H_5I + CO_2 \qquad (3)$$

$$2I\cdot \longrightarrow I_2 \qquad (4)$$

If we assume that the hypoiodite titrates along with iodine we may write

$$z = [C_6H_5COOI]$$

$$x = [I_2] + z$$

$$\frac{dx}{dt} = k_1[P] - k_3z \qquad (5)$$

$$\frac{dx}{dP} = \frac{k_3}{k_1}\frac{z}{[P]} - 1 \qquad (6)$$

$$\frac{dz}{dP} = \frac{k_3}{k_1}\frac{z}{[P]} - 2 \qquad (7)$$

Equation (6) shows that the mechanism is consonant with the increase in x during the early stages of a run before $z/[P]$ reaches its maximum value. It is also apparent that equations (6) and (7) would serve as a further test of the proposed mechanism if z could be evaluated with sufficient precision. We have attempted to calculate these values by means of the relationships

$$[I_2] = [I_2]_0 - ([P]_0 - [P])/2 \qquad (8)$$

$$z = x - [I_2]_0 + ([P]_0 - [P])/2 \qquad (9)$$

The values of z calculated by the application of equation (9) to our data were plotted against P. The resulting slopes were taken and plotted against the ratio $z/[P]$. Only rough values of 8–20 for k_3/k_1 could be obtained. At least two factors contribute to the looseness of this fit. First, the absolute values of the hypoiodite concentrations reached a maximum of only 0.006 molar in the most concentrated solution (Run 18). Relative to the iodine and peroxide concentrations this is a small amount so the calculated values of z represented small differences between two analytical values, with whatever inherent errors are involved in them. A second error arises from our assumption that the stoichiometry of the reaction is exactly that to be expected from equations (1) to (4). Actually slightly less than a mole of iodine was consumed per mole of peroxide. This means that during the later stages of a run the iodine concentrations calculated by equation (8) are in error by an amount which is large in comparison with concentrations of hypoiodite. For the late points z even appeared to be negative.

Although it is strictly incorrect to extend the steady state assumption to benzoyl hypoiodite which is postulated to be accumulating to an analytically significant concentration, it is safe to assume, since z never becomes very large, that its rates of formation and disappearance must be of the same order of magnitude over the course of most of a run. Since this is equivalent to the assumption that the value of the net rate of change of z is quite small, it is easily shown that dx/dP should approach one. The last column of Table II records the slopes determined during the later stages of the various runs. These values do indeed appear to approach one at high peroxide concentrations. The value of 1.13 from run 11 is unexpectedly high but this may be due in part to experimental error. Since the values of the ratio, $z/[P]$ were found to be approximately 0.07 to 0.10 over a considerable period of time in all the runs the "pseudo steady state" relationship utilized above

$$z \cong 2k_1[P]/k_3 \qquad (10)$$

leads to values of 20–30 for the ratio k_3/k_1. This agrees as well as could be expected with the values determined by use of equations (7) to (9).

The isolation of a 3.1% yield of phenyl benzoate from the reaction without water is further indication that the mechanism is not correct in all details. Since this substance was not found when water was present it is likely that it is formed from the hypoiodite. There are a number of paths by which such a transformation might take place. Three of these may be formulated as

$$\text{Path A} \quad 2C_6H_5CO_2I \longrightarrow C_6H_5CO_2C_6H_5 + CO_2 + I_2 \qquad (11)$$

$$\text{Path B} \quad C_6H_5CO_2\cdot + C_6H_5CO_2I \longrightarrow C_6H_5CO_2C_6H_5 + CO_2 + I\cdot \qquad (12)$$

$$\text{Path C} \quad 2C_6H_5CO_2I \rightleftarrows 2C_6H_5CO_2\cdot + I_2 \qquad (13)$$

$$C_6H_5CO_2\cdot \longrightarrow C_6H_5\cdot + CO_2 \qquad (14)$$

$$C_6H_5\cdot + C_6H_5CO_2I \longrightarrow C_6H_5CO_2C_6H_5 + I\cdot \qquad (15)$$

It is obvious that in Path C the ester could be produced by reaction (12) as well as through the sequence (14) and (15). The difference between the two alternatives lies in the fact that the quantitative conversion to benzoic acid in the presence of water disallows reaction (14) unless the formation of hypoiodite is reversible. The reversible formation of benzoate radicals from the hypoiodite also affords an alternative to reaction (3) for the conversion of the latter to iodobenzene. This product might be formed either by the direct interaction of benzoate with iodine[12] or from phenyl radicals produced in reaction (14). Numerous approaches suggest themselves as possible methods of determining whether or not this equilibrium is established. However, it is our belief that hypoiodites are also formed in the reaction of silver salts of carboxylic acids with iodine. Since other groups[13,14] are currently engaged in the study of the mechanism of the latter reaction we do not intend to pursue the problem further.

Not only can the results of the present investigation be correlated with those of the earlier study, but the conclusions that were drawn then may now be extended. It was found in the previous work that a maximum of 10% of the theoretical amount of carbon dioxide was produced in reaction (1). We have now demonstrated, by the quantitative conversion of peroxide to benzoic acid in the presence of iodine and water, that decarboxylation in the primary process of thermal decomposition is completely negligible.[15]

Summary

The decomposition of benzoyl peroxide in carbon tetrachloride in the presence of iodine has been studied by product analysis and kinetics.

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(12) Bartlett and Kwart (This Journal, **72**, 1051 (1950)) have presented evidence that reactions of radicals with iodine are second order with respect to iodine and produce $I_3\cdot$ rather than iodine atoms. The order of such reactions in our work cannot be estimated so we have chosen a more conventional formulation for the sake of simplicity.

(13) Arnold and Morgan, *ibid.*, **70**, 4248 (1948).

(14) Arcus, Campbell and Kenyon, *Nature*, **163**, 287 (1949).

(15) Cosgrove and Waters (*J. Chem. Soc.*, 3189 (1949)) have recently drawn similar conclusions as the result of a study of the decomposition of benzoyl peroxide in the presence of phenols. However, it is likely that in their experiments most of the peroxide was destroyed in a chain reaction and that the results do not necessarily reflect the chemistry of the primary process in thermal decomposition. Cass (This Journal, **68**, 1976 (1946)) has reported similar results in reactions in which induced decompositions were predominant.

The rate of peroxide decomposition is constant in homogeneous solution and is independent of the iodine concentration. The apparent relative rate of iodine consumption per mole of peroxide consumed is a complex function of the initial concentrations. Evidence that benzoyl hypoiodite accumulates in solution is discussed.

AMES, IOWA RECEIVED APRIL 5, 1950

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY OF CALIFORNIA, LOS ANGELES]

The Photolysis of Aliphatic Aldehydes. XIII. Acetaldehyde-*d*

BY F. E. BLACET AND R. K. BRINTON[1]

Work reported earlier[2,3] indicated that the absorption of ultraviolet light by acetaldehyde molecules may initiate either one of two primary reactions leading to decomposition.

$$CH_3CHO + h\nu \longrightarrow CH_4 + CO \quad (1a)$$
$$CH_3CHO + h\nu \longrightarrow CH_3 + CHO \quad (1b)$$

The intramolecular process (1a) produces the main decomposition products, methane and carbon monoxide directly, while the split into methyl and formyl radicals (1b) must be followed by various secondary reactions which will explain the formation of ethane and carbon monoxide as well as the secondary products, hydrogen, diacetyl, glyoxal, and formaldehyde, reported by Blacet and Blaedel.[4] These authors discussed the radical decomposition mechanism in the temperature range 20 to 100° as a short chain process involving the methyl radical.

$$CH_3 + CH_3CHO \longrightarrow CH_4 + CH_3CO \quad (3)$$
$$CH_3CO \longrightarrow CH_3 + CO \quad (4)$$

The combination of various radicals present in the system satisfactorily explains diacetyl, glyoxal, and formaldehyde production. The formation of hydrogen is possibly an interaction of formyl radicals with acetaldehyde.

$$CHO + CH_3CHO \longrightarrow H_2 + CO + CH_3CO \quad (2)$$

The work presented in this paper represents an attempt to clarify further the secondary radical reactions by a study of the photolysis of acetaldehyde-*d*, CH_3CDO. By analogy the primary steps are

$$CH_3CDO + h\nu \longrightarrow CH_3D + CO \quad (1aD)$$
$$CH_3CDO + h\nu \longrightarrow CH_3 + CDO \quad (1bD)$$

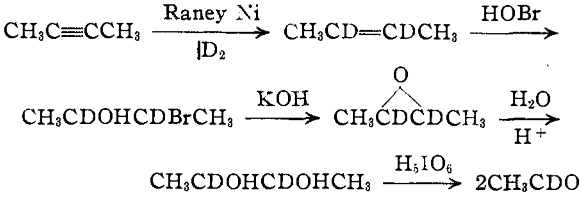
The propagation of the chain mechanism should proceed by either the capture of the acyl deuterium atom

$$CH_3 + CH_3CDO \longrightarrow CH_3D + CH_3CO \quad (3aD)$$

followed by (4) or the capture of the methyl hydrogen atom followed by a rearrangement and dissociation also into carbon monoxide and a methyl radical. A chain involving acyl hydrogen capture should lead to pure methane-*d*, CH_3D, while one brought about by methyl hydrogen capture would yield mixtures of methane and methane-*d* at low temperatures (20–100°) where the chain lengths are short, and pure methane-*d* at high temperatures where the primary yield of (1aD) is small compared to the total methane produced. The result of both chain mechanisms operating simultaneously would of course result in mixtures of methane-*d* and methane over the whole temperature range. It was thought that analysis of the photolysis products for the relative amounts of methane and the various heavy methanes and also for the other deuterated products would possibly yield valuable evidence as to the course of the secondary radical reactions.

Experimental Procedures and Results

Acetaldehyde-*d* used in the photolysis experiments was synthesized by the following reaction sequence



$$CH_3C{\equiv}CCH_3 \xrightarrow[D_2]{\text{Raney Ni}} CH_3CD{=}CDCH_3 \xrightarrow{HOBr}$$
$$CH_3CDOHCDBrCH_3 \xrightarrow{KOH} CH_3\overset{O}{CDCD}CH_3 \xrightarrow[H^+]{H_2O}$$
$$CH_3CDOHCDOHCH_3 \xrightarrow{H_5IO_6} 2CH_3CDO$$

The initial catalytic half reduction was carried out in a closed system by circulating deuterium gas (99.8 mole % D_2) at about 2 atm. pressure through a solution of the butyne in ether solvent. In a representative reduction 5090 ml. of deuterium was added to 10.9 g. of 2-butyne and 0.5 g. of Raney nickel catalyst[5] in 25 ml. of ether during a four-hour period. Solvent and hydrocarbon materials carried out of the solution by the 200 ml./min. deuterium gas stream were returned by a cold finger condenser at −80°. The combined yields of several reductions were converted to acetaldehyde by methods previously described.[6,7,8] The aldehyde yield from 2-butyne was 27% of the theoretical value. Purification of the acetaldehyde was effected by conversion to the alde-

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[1] Division of Chemistry, University of California, Davis, California.

[2] F. E. Blacet and J. D. Heldman, THIS JOURNAL, **64**, 889 (1942).

[3] F. E. Blacet and D. E. Loeffler, *ibid.*, **64**, 893 (1942).

[4] F. E. Blacet and W. J. Blaedel, *ibid.*, **64**, 3374 (1940).

[5] L. W. Covert and H. Adkins, *ibid.*, **54**, 4116 (1932).

[6] S. Winstein and R. E. Buckles, *ibid.*, **64**, 2784 (1942).

[7] C. E. Wilson and H. J. Lucas, *ibid.*, **58**, 2399 (1936).

[8] E. L. Jackson, "Organic Reactions," Vol. II, John Wiley and Sons, Inc., New York, 1944, p. 341.