

(P, As, Sb, Bi) $X_2$ ,  $R_2$  (S, Se, Te) $X_2$ , and  $R_1X_2$ , the halogen atoms would occupy apical positions in a trigonal bipyramidal structure at distances from the central atom which are greater than for normal M-X bonds. It is also reasonable to expect that all of these molecules show more or less tendency to dissociate in solution, giving the free halogen,  $X_2$ , as one product. A number of these dissociation constants are now being determined in this Laboratory.

### Summary

1. Spectrophotometric studies of diphenylselenium dibromide and diphenylselenium diiodide indicate that these substances dissociate in car-

bon tetrachloride solution into diphenylselenium and the free halogen.

2. Dissociation constants for both compounds have been determined at  $26^\circ \pm 1^\circ$  at which  $K_1 = [(C_6H_5)_2Se][Br_2]/[(C_6H_5)_2SeBr_2] = 5.02 \times 10^{-4}$ ; and  $K_2 = [(C_6H_5)_2Se][I_2]/[(C_6H_5)_2SeI_2] = 3.60 \times 10^{-2}$ .

3. Molar extinction coefficients for diphenylselenium, diphenylselenium dibromide and diphenylselenium diiodide are shown in Table I and in Fig. 1.

4. An accurate volumetric procedure for the determination of diarylselenium dihalides is described.

LOS ANGELES, CAL.

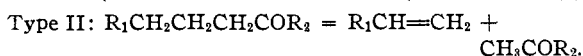
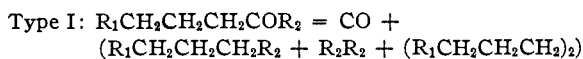
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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ROCHESTER]

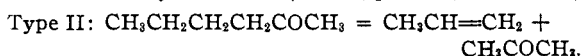
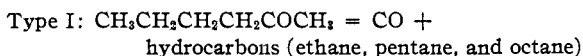
## Photochemical Studies. XXXV. The Photochemical Decomposition of *n*-Butyl Methyl Ketone

BY WALLACE DAVIS, JR.,<sup>1</sup> AND W. ALBERT NOYES, JR.

The photochemical decompositions of *n*-butyl methyl ketone and of other ketones containing multi-carbon alkyl groups attached to the carbonyl have been investigated by Norrish and his co-workers.<sup>2</sup> On the basis of their results these authors have suggested that such ketones undergo two types of decomposition, which they designate as I and II



Thus for *n*-butyl methyl ketone the reactions would be



The theoretical discussion of this photochemical reaction will be reserved for a later article in which further data will be presented. It may be pointed out in passing that Norrish and his co-workers have come to the conclusion that the

(1) Eastman Kodak Company Fellow in Photochemistry at the University of Rochester, 1941-1942. Mr. Davis resigned from this Fellowship in February, 1942, to accept a research position connected with National Defense, and being unable to continue the problem, the preliminary results he obtained are being published at the present time.

(2) C. H. Bamford and R. G. W. Norrish, *J. Chem. Soc.*, 1531 (1938).

Type I reaction probably proceeds by a free radical mechanism whereas Type II proceeds in a single step leading to the final products. Others have discussed methods by which such a one-step process could occur,<sup>3</sup> and still others are inclined to the belief that Type II can also be explained by a free radical mechanism.<sup>4</sup>

Since acetone, if formed, would decompose photochemically to give carbon monoxide, any photochemical experiment leading to a large percentage decomposition of *n*-butyl methyl ketone would yield carbon monoxide as a secondary product. Furthermore, Norrish found that the yield of carbon monoxide was low. Since the stability of RCO radicals may vary markedly with the temperature, the quantum yields of all the products should be determined over a wide range of conditions.

The objects of the present investigation were as follows: (1) to apply and if necessary devise methods for the micro-analysis of the products formed during the photochemical decomposition of *n*-butyl methyl ketone so that the initial stages of the reaction could be investigated; (2) to determine the quantum yields of the various prod-

(3) F. O. Rice and E. Teller, *J. Chem. Phys.*, **6**, 489 (1938).

(4) G. B. Kistiakowsky; for mention see V. R. Ellis and W. Albert Noyes, Jr., *THIS JOURNAL*, **61**, 2495 (1939); see W. Albert Noyes, Jr., and P. A. Leighton, "The Photochemistry of Gases," Reinhold Publishing Corporation, New York, N. Y., 1941, p. 365.

TABLE I  
ANALYSIS OF DECOMPOSITION PRODUCTS OF METHYL *n*-BUTYL KETONE  
(Runs without filters on mercury arc)

1 Run	2 Press. of ketone, mm.	3 Exposure time, min.	4 Temp., per <i>t</i> , °C.	5 Liquid nitrogen fraction (-195°C.), moles × 10 <sup>-3</sup>	6 <i>n</i> -Pentane fraction (-130° or lower), moles × 10 <sup>-3</sup>	CuO combustion tube: ca 200° Anal. of liq. N <sub>2</sub> frac.	
						7 <sup>a</sup> C <sub>2</sub> H <sub>6</sub> -Liq. N <sub>2</sub> frac., moles × 10 <sup>-3</sup>	8 CO <sub>2</sub> - <i>n</i> -pentane frac., moles × 10 <sup>-3</sup>
1	12	15	24	12.3	...	4.4	5.0
2	10	45	24	58.5	620	5.7	...
3	5	30	24	8.6	97.5	0.9	6.6
4	13	80	24	48.0	...	6.2	41.1
5	7	60	28	17.2	170	1.6	13.1
6	18	30	24	...	151	...	...
7	10	60	28	16.3	227	1.4	13.4
8	12	60	26	45.3	573	...	...
9	11	60	23	43.5	535	...	...
10	12	60	24.5	23.8	397	2.4	19.6
11	12	60	24	27.0	258	2.3	21.3

<sup>a</sup> The copper oxide does not oxidize hydrocarbons, so that this column represents such hydrocarbons (mostly ethane) which can be removed by the Toepler pump when the products are condensed with liquid nitrogen.

Hot Pt wire combustion tube: ca >600°

Analysis of <i>n</i> -pentane Fraction (O <sub>2</sub> combustion)		9/6 Moles O <sub>2</sub> used per mole of <i>n</i> -pentane fraction of photodecomp. products		10/6 Moles CO <sub>2</sub> formed from comb. of <i>n</i> -pentane frac. per mole of <i>n</i> -pentane frac.		2 × 11/6 g. atoms H <sub>2</sub> per mole of <i>n</i> -pentane fraction	6/5 Ratio of <i>n</i> -pentane fraction to liq. N <sub>2</sub> fraction	6/8 Ratio of <i>n</i> -pentane fraction to CO <sub>2</sub> in liq. N <sub>2</sub> fraction	8/5 × 100 % CO <sub>2</sub> in liq. N <sub>2</sub> fraction
...	...	...	...	...	...	...	...	...	40
...	...	...	...	...	...	...	10.6	...	...
...	...	...	...	...	...	...	11.3	14.8	77
...	...	...	...	...	...	...	...	...	86
...	...	...	...	...	...	...	9.9	13.0	76
685	465	441	4.4	3.08	5.86	...	...	...	...
1045	690	708	4.6	3.04	6.24	13.9	16.9	82	...
...	...	...	...	...	...	12.7	...	...	...
...	...	...	...	...	...	12.3	...	...	...
...	...	...	...	...	...	16.7	20.2	82	...
1210	863	695	4.7	3.34	5.4	9.6	12.1	79	...

ucts under diverse experimental conditions to aid in the elucidation of the mechanism. Much of (2) was not accomplished, and the discussion will be postponed until a later date.

### Experimental

Eastman Kodak Company *n*-butyl methyl ketone (b. p. approx. 127°) was converted to the semicarbazone and precipitated from a mixture of distilled water and ethyl alcohol; 250 cc. of water was added to 30 cc. of ketone and ethyl alcohol added until solution was complete. Sodium acetate and semicarbazide hydrochloride were added in slight excess of equivalent amounts and the derivative precipitated, m. p. 123°. The derivative was recrystallized from water and ethyl alcohol, hydrolyzed by refluxing with 15% sulfuric acid, and then distilled. The resulting product was dried with anhydrous magnesium sulfate, *n*<sup>25D</sup> 1.4003. The ketone was stored in the dark, under vacuum (usually at -77°).

In the first series of runs unfiltered light from a high pressure mercury arc lamp was used. In the second series the following filter was used to isolate the 3130 Å. line: (1) 5-cm. quartz cell filled with a solution made by adding

14 g. of CoSO<sub>4</sub>·7H<sub>2</sub>O, 46 g. of NiSO<sub>4</sub>·6H<sub>2</sub>O to 330 cc. of water; (2) a 0.5-cm. cell filled with solution containing 10 g. of potassium acid phthalate per liter; (3) blue glass to remove the visible mercury lines.

After exposure, the reaction mixture was condensed with liquid nitrogen and the residual gases (CO, H<sub>2</sub>, CH<sub>4</sub>, part of the C<sub>2</sub>H<sub>6</sub>) were removed by a Toepler pump. This part was further fractionated and analyzed. It was always small. Next the gases uncondensed by a *n*-pentane wash at temperatures from -130 to -145° were removed and analyzed. As shown in the table this fraction consisted mostly of a compound of empirical formula C<sub>3</sub>H<sub>6</sub>, presumably propylene. Finally, a fraction removed at -77° gave fair agreement for the empirical formula of acetone. This agreement was obtained by measuring both carbon dioxide produced, water formed, and oxygen consumed during the burning of this fraction. It should be emphasized that the presence of acetone in the quantities indicated has not been definitely established. Difficulty was experienced in removing all of the acetone. The first pump-fulls gave a good analysis, but small amounts of material kept coming over for long periods, and these gave spurious results. If Type II decomposition occurs and the amount of propylene is really equal to

TABLE II  
ANALYSIS OF DECOMPOSITION PRODUCTS OF METHYL *n*-BUTYL KETONE  
(Runs with filters on mercury arc)

1 Run	2 Press. of ketone, mm.	3 Exposure time, min.	4 Temp., °C.	5 Liquid nitrogen fraction (-195°) moles × 10 <sup>-3</sup>	6 Fractions taken off after liq. N <sub>2</sub> fraction, moles × 10 <sup>-3</sup>	CuO combustion tube: ca 200° Anal. of liq. N <sub>2</sub> frac.	
						7 <sup>b</sup> C <sub>2</sub> H <sub>6</sub> -Liq. N <sub>2</sub> frac. moles × 10 <sup>-3</sup>	8 CO <sub>2</sub> - <i>n</i> -pentane frac. moles × 10 <sup>-3</sup>
12	8	220	24	1.24	59.0 (-130°)	...	...
13	12	720	24	4.85	75.0 (-145°) 265.5 (-130°) 23.6 (-115°) 69.0 (- 80°) 111.0 (- 77°) <sup>a</sup> 111.0 (- 77°)	1.1	3.0
14	12	240	24	1.51	47.0 (-130°)	...	...
15	7	245	26	1.1	38.7 (-130°)	...	...

<sup>a</sup> All this fraction not taken because gas was coming off dry-ice very slowly and evidently very impure. <sup>b</sup> The copper oxide does not oxidize hydrocarbons so that this column represents such hydrocarbons (mostly ethane) which can be removed by the Toepler pump when the products are condensed with liquid nitrogen.

Hot Pt. wire combustion tube: ca. >600°  
near wire

Analysis of fractions taken off after removal of liq. N <sub>2</sub> fraction			9/6 Moles O <sub>2</sub> used per mole of frac- tion burned on Pt	10/6 Moles CO <sub>2</sub> formed per mole of fraction burned on Pt	2 × 11/6 g. atoms H <sub>2</sub> per mole of fraction burned on Pt	6/5 Ratio of Σ fraction taken off after liq. N <sub>2</sub> fraction to liq. N <sub>2</sub> fraction	6/8 Ratio of Σ of fractions taken after liq. N <sub>2</sub> fraction to CO <sub>2</sub> in liq. N <sub>2</sub> fraction	8/5 × 100 % CO <sub>2</sub> in liq. N <sub>2</sub> fraction
9 O <sub>2</sub> used in combustion, moles × 10 <sup>-3</sup>	10 CO <sub>2</sub> formed, <i>n</i> -pentane fr., moles × 10 <sup>-3</sup>	11 H <sub>2</sub> O formed (by diff.), moles × 10 <sup>-3</sup>						
313	213	200	5.3	3.61	6.78	48	...	...
334	222	224	4.45	2.96	5.98			62
1290	840	900	4.86	3.16	6.73			
111	68.5	85	4.7	2.9	7.2			
279	206	146	4.04	2.99	4.2+2=6.2			
460	348	224	4.14	3.14	4.04+2=6.04			
...	364	...	...	3.28	...			
...	...	...	...	...	...	31	...	...
...	...	...	...	...	...	35	...	...

the amount of acetone, only about 75% of the acetone is recovered from the reaction mixture.

Two attempts were made to estimate the quantum yields, using a galvanometer and photocell circuit calibrated for another research. The values  $\Phi_{C_2H_6} = 0.6$  and  $\Phi_{CO} = 0.15$  should be given little weight, and further data will be presented in a later article.

### Conclusions

The photochemical decomposition of *n*-butyl methyl ketone at room temperature (23–28°) at pressures from 5 to 13 mm. yields mainly compounds having the empirical formula C<sub>3</sub>H<sub>6</sub> and C<sub>3</sub>H<sub>6</sub>O. This is true for unfiltered radiation of the mercury arc and for approximately monochromatic 3130 Å. radiation.

Small amounts of carbon monoxide are produced, the relative amount being greater for the unfiltered radiation than at 3130 Å. However, the amount of decomposition was several fold larger for the unfiltered radiation. In no case was more than a few per cent. of the parent ketone decomposed, and for the unfiltered radiation the amount did not exceed a few tenths of a per cent.

Some doubt may be expressed as to whether any carbon monoxide is formed by the decomposition of *n*-butyl methyl ketone. Carbon monoxide might be formed entirely from the decomposition of acetone formed in the initial reaction.

ROCHESTER, NEW YORK

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