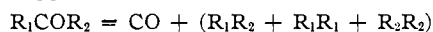


[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF ROCHESTER]

Photochemical Studies. XXXVI. Quantum Yields during the Photochemical Decomposition of *n*-Butyl Methyl Ketone

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In a recent paper¹ it was shown that the photochemical decomposition of *n*-butyl methyl ketone yields very small amounts of carbon monoxide. In fact the amount is so small during the early stages of the reaction that some doubt exists as to whether any of the decomposition of this compound proceeds according to the Type I mechanism suggested by Norrish and his co-workers²



On the other hand, some evidence exists for the Type II decomposition into propylene and acetone, a process which Bamford and Norrish² have suggested as a single step primary process.

The present work was undertaken with a view to determining the quantum yields of formation of the various products from *n*-butyl methyl ketone under a wide variety of experimental conditions so that further information concerning the mechanism of this reaction could be obtained.

Experimental

The apparatus was designed so that very small amounts of gas could be measured and analyzed. The apparatus for analysis was similar to that described by Manning.³ The apparatus was of Pyrex, and mercury cut-offs were used exclusively so that no stopcock grease was present in any part of the system.

The products of the reaction were removed by means of a Toepler pump while the methyl butyl ketone was condensed by various cooling agents. Following removal of the products they were analyzed either by the partial combustion method described by Manning or by obtaining vapor pressure—temperature curves following the method of Sebastian and Howard.⁴

The methyl butyl ketone (Eastman Kodak Co.) was further purified by repeated distillation, each time discarding the first and last fractions, and dried by standing over calcium chloride. Purity was demonstrated by measuring the refractive

index. The value obtained was 1.3969 (25°) as compared with 1.39694 (17.4°) given in the "International Critical Tables."

The light source used in most of the experiments was a Hanovia 150-watt uviarc. Filter solutions in quartz cells were used to obtain the desired wave length. For 3130 Å., a 5-cm. path of a solution of 14 g. of CoSO₄·7H₂O and 46 g. of NiSO₄·6H₂O in 330 cc. of water and a 0.5-cm. path of a solution of 10 g. of potassium acid phthalate in one liter of water was used. The purity of this line has been estimated to be about 90%,⁵ and was qualitatively demonstrated by making photographs. The source hereafter described as "2537 Å." was actually the range 2320–2804 Å. and was obtained by using the chlorine filter described by Villars.⁶

Light intensity was measured by means of a photoelectric cell having a quartz window. The photoelectric current was measured by a Leeds and Northrup mirror-type galvanometer. The scale was placed approximately two meters away from the mirror, and deflection in cm. read through a telescope. A uranyl oxalate actinometer was used to calibrate the photocell. The actinometer solution was 0.01 molar uranyl sulfate and 0.05 molar oxalic acid dissolved in water. A 2-ml. sample and 5-mm. path length were used. Exposures were about twelve hours in length. The oxalate was titrated before and after exposure with 0.01 normal potassium permanganate solution. Reflection from the face of the oxalate cell was corrected for by the equation

$$I = I'/0.960, \text{ for } 3130 \text{ \AA.}$$

$$I = I'/0.957, \text{ for } 2537 \text{ \AA.}$$

I is quanta per second falling on the cell and *I'* is quanta per second calculated from oxalate decomposed. The calibration gave the following results

Wave length, 3130 Å.

Normality of KMnO₄ = 0.0105

Oxalate used = 4.49 cc. KMnO₄

Quantum yield = 0.567

Time exposed = 4.37 × 10⁴ sec.

Galvanometer deflection in (second)(cm.) = 29.0 × 10⁵

(5) H. L. Bäckström, *Naturwissenschaften*, **23**, 251 (1933).

(6) D. S. Villars, *THIS JOURNAL*, **48**, 1874 (1926).

(7) G. S. Forbes and L. J. Heidt, *ibid.*, **56**, 2363 (1934).

(1) W. Davis, Jr., and W. A. Noyes, Jr., *THIS JOURNAL*, **64**, 2676 (1942).

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

(3) W. M. Manning, *THIS JOURNAL*, **56**, 2589 (1934).

(4) J. J. S. Sebastian and H. C. Howard, *Ind. Eng. Chem., Anal. Ed.*, **6**, 172 (1934).

$$\frac{\text{Quanta/sec. per cm. deflection} = (0.0105)(4.49)(6.03 \times 10^{23})}{(1000)(2)(0.56)(0.960)(2\text{E}.0 \times 10^8)} = 0.91 \times 10^{13} \text{ quanta/sec. per cm.}$$

Wave length, 2537 Å.

Normality of $\text{KMnO}_4 = 0.0105$

Oxalate used = 4.47 cc. KMnO_4

Quantum yield = 0.61⁷

Galvanometer deflection in (second)(cm.) = 4.02×10^6

Time exposed = 4.52×10^4 sec.

$$\frac{\text{Quanta/sec. per cm. deflection} = (4.47)(0.0105)(6.03 \times 10^{23})}{(1000)(2)(0.957)(0.61)(4.02 \times 10^6)} = 0.60 \times 10^{13} \text{ quanta/sec. per cm.}$$

Results

The products found were ethane, propylene, acetone, methyl ethyl ketone and biacetyl. There are also reasons to suppose propane is produced, which will be presented later.

Liquid nitrogen was placed first on the reaction system as a cooling agent, -195° , and the available product was transferred to the McLeod gage system by means of a Toepler pump. Within the limits of accuracy of the combustion analysis this product was a two-carbon hydrocarbon (see Table I), and hence could be ethane or a mixture of ethane and ethylene.

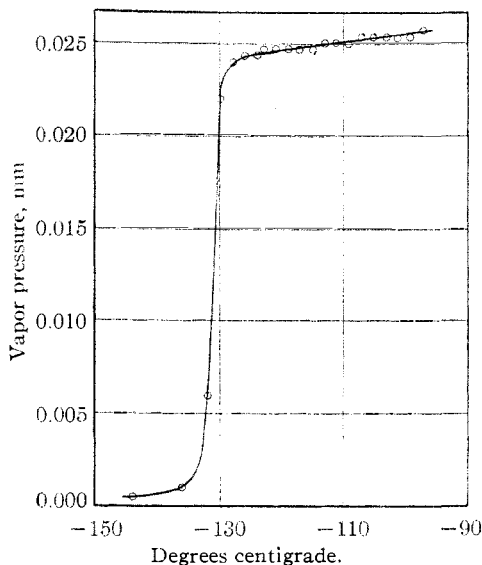


Fig. 1.—Propylene fraction.

Pentane mush (-131°) was then used as a cooling agent and the available product pumped off, measured and burned. The fraction thus obtained is believed to contain propylene mixed with propane. The combustion analysis agrees well with propylene (see Table I) and propylene is known to exert appreciable vapor pressure at -131° .⁴ Further, propylene was identified by

TABLE I

COMBUSTION ANALYSES OF PRODUCTS

These analyses are a representative fraction of the large number made. All pressures are given in McLeod gage units, which when multiplied by 6.52×10^{-5} gives pressure in mm. It should be noted that the methyl ethyl ketone was contaminated by biacetyl.

Temp. of removal, °C.	(Probable substance burned)	Amount	Carbon dioxide theoret.	Carbon dioxide exp.	Oxygen theoret.	Oxygen exp.
-195	Ethane	106	212	193	371	293
-195	Ethane	107	214	207
-195	Ethane	53	106	100	186	111
-131	Propylene	383	1149	1099	1724	1662
-131	Propylene	183	549	550	824	856
-120	Acetone	294	882	970	1176	1452
-78	Dry-ice ⁴	75	300	292	413	464
-78	Fraction	37	148	140	204	251
-78	Fraction	93	372	368	512	565

⁴ Acetone was removed as described in the Experimental Part before this analysis was made.

Norrish⁸ as one of the principal products of the reaction. This fraction may include propane as well as propylene, since the accuracy of the combustion analysis is too low to exclude propane. A Sebastian and Howard⁴ curve was made for this fraction, and a typical experiment is shown in Fig. 1. Since the curve rises steeply without the presence of an intermediate plateau, the propylene fraction could be contaminated by propane, but by no other substance in an appreciable amount.

Dry-ice in alcohol (-78°) was next used as a

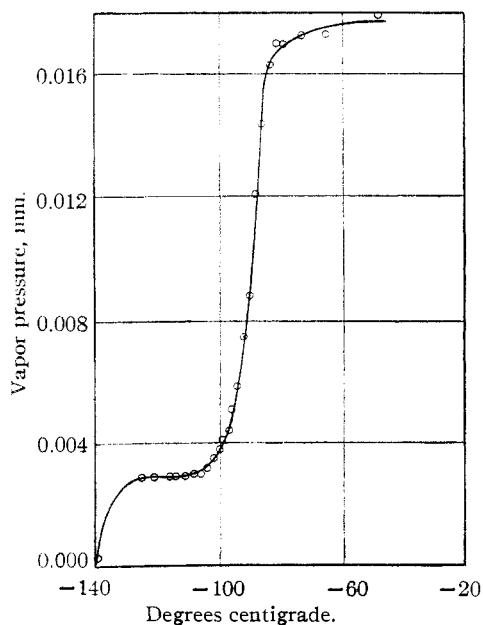


Fig. 2.—Dry-ice fraction.

(8) C. H. Bamford and R. G. W. Norrish, *J. Chem. Soc.*, 1544 (1938).

cooling agent, and the fraction obtained can be seen to contain at least two substances by inspection of Fig. 2. The temperature was allowed to rise to -125° in the McLeod gage system, and a sample of the lower boiling component was pumped to the combustion chamber and combusted. It was found to contain 3 carbon atoms per molecule (Table I). This small amount of material may be either acetone or propane or propylene not removed in the previous fraction.

In other runs the lower boiling component of the dry-ice fraction was pumped off and discarded. A Toepler pump was always used for this purpose. The higher boiling fraction was then pumped into the combustion chamber and analyzed. It was found to contain 4 carbon atoms per molecule. Possibilities would be butane, methyl ethyl ketone, and biacetyl.

Butane is excluded since it has an appreciable vapor pressure at the temperature of pentane mush,⁴ and would have come off with the pentane mush fraction.

To detect the presence of biacetyl, the nickel dimethylglyoxime test was used. When the light source was used without filters and a twelve-hour run was made, about 0.39 mm. of the dry-ice fraction could be obtained in the 428 cc. of the McLeod system. If one-third of this were biacetyl, there would be 3×10^{-6} mole of biacetyl, or about one one-hundredth of a drop of biacetyl available for the test. To see whether this small amount could be detected, tests were made on known biacetyl. A procedure which was successful was as follows.

One drop of biacetyl was dissolved in 50 cc. of water and then 0.5 cc. of this solution placed in a small test-tube. Twenty drops of a solution of 3 g. of hydroxylamine hydrochloride and 5 g. of potassium hydroxide in 25 cc. of water and 25 cc. of ethyl alcohol were then added, and the solution shaken. Then two drops of a solution of 3 g. of nickel sulfate in 50 cc. of water and 50 cc. of 20% acetic acid were run down the side of the slanted tube carefully so that the nickel sulfate solution formed a bottom layer. The pink nickel dimethylglyoxime precipitate slowly appeared at the boundary of the two layers. This test was also shown to be capable of detecting one two-hundredth of a drop in 0.5 cc. A long run was made as described above, the dry-ice fraction condensed into a trap by liquid air, the trap was removed from the system and the contents dis-

solved in 0.5 cc. of water. Application of the above test gave the pink precipitate and showed that biacetyl was produced in the reaction. This is only a qualitative test and does not show what portion of the dry-ice fraction is composed of biacetyl.

The bulk of this fraction could not be biacetyl, since its vapor pressure, as seen from Fig. 2, is already 0.012 mm. at -85° while the vapor pressure of biacetyl is only 0.01 at -70° .⁹ Since butane is excluded, the only remaining possibility having 4 carbon atoms is methyl ethyl ketone. Other possible 4 carbon compounds would have either too high or too low a vapor pressure to be included in the dry-ice fraction. On these grounds the assumption was made that the greater part of the dry-ice fraction was methyl ethyl ketone.

The quantum yields were calculated in the usual way using the uranyl oxalate actinometer as described by Forbes and Heidt.⁷ The accuracy is relatively low because of the small amounts of products, but the general trend of the results is clearly indicated.

The results may be summarized as follows:

1. The quantum yield of the propane-propylene fraction is about 0.34 at 27° and is nearly independent of the intensity and the pressure.
2. The quantum yield of the propane-propylene fraction increases slightly with temperature, although this variation is not much greater than experimental error.
3. The quantum yield of the propane-propylene fraction is the same at 3130 Å. as at 2537 Å. within experimental error.
4. The quantum yield of the acetone, methyl ethyl ketone and biacetyl fraction is about 0.26 at 3130 Å. and 27° and is independent of the intensity. The yield increases slightly as the wave length is decreased to 2537 Å.
5. The "methyl ethyl ketone" yield constitutes most of the methyl ethyl ketone-biacetyl-acetone fraction and is a little greater than 0.2. It is practically independent of temperature, wave length, intensity and pressure.
6. The ethane quantum yield is about 0.1, is independent of intensity and wave length but increases slightly with temperature.
7. The carbon monoxide quantum yield is always very small although it does seem to increase slightly with temperature.

(9) V. R. Ellis, *THIS JOURNAL*, **60**, 1864 (1938).

8. Summarizing, the quantum yields are low and nearly independent of all variables, the only exceptions being yields of carbon monoxide and of ethane which increase with the temperature.

It must be emphasized that final identification of methyl ethyl ketone has not been accomplished.

Discussion of Results

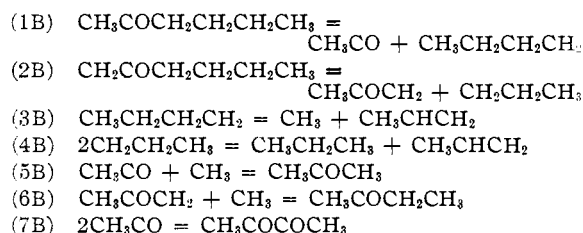
It has been suggested¹⁰ that the decomposition of *n*-butyl methyl ketone might be explained entirely on a free radical basis. The data presented herein indicate that there may be some formation of acetyl radicals, but the small yield of carbon monoxide indicates that this is not extensive. The increase in yield of carbon monoxide with temperature may be due to some primary decomposition into butyl and acetyl radicals. It does not seem possible to explain the small yield of carbon monoxide on the basis of absorption by acetone which is formed in the reaction, although the formation of biacetyl might be ascribed to this step since a positive test for this substance was obtained as a result of long exposures.

The relatively small variation of all quantum yields as a function of all variables might indicate a single step decomposition into final products. Two arguments may be advanced against this assumption: (1) the propylene yield is higher than the acetone yield; (2) there is something present which has been referred to as methyl ethyl ketone. It must be emphasized that the identification of this latter substance is not positive and that it is not useful at the present time to enter into a detailed discussion of the possible mechanism of its formation.

It is, of course, possible to devise a free radical mechanism which would account for all of the possible products and still make the quantum yields relatively insensitive to the various variables. If methyl ethyl ketone is a principal product such a free radical mechanism must involve the combination of acetyl and methyl radicals

(10) See Noyes and Leighton, "The Photochemistry of Gases," The Reinhold Publishing Corporation, New York, N. Y., 1941, p. 365

to give this compound. The following equations account for many of the facts.



It must be emphasized, however, that no proof exists for mechanisms of this type and as far as the data are concerned, we are unable to distinguish between a single step process and a free radical mechanism. Since acetone is formed to a lesser extent than propylene, a simple one step process evolving these products scarcely seems to be the only thing which can take place. It is suggested that further work using other types of technique will be necessary before the final establishment of the mechanism. The small yield of carbon monoxide would seem to indicate the presence of relatively few acetyl radicals, but that some are present is indicated by the definite increase in carbon monoxide yield with temperature.

The authors wish to express their appreciation to Mr. Jerome J. Howland, Jr., who determined the increase in quantum yield of carbon monoxide formation with temperature.

Summary

1. The quantum yields of formation of various products of the decomposition of *n*-butyl methyl ketone have been obtained as a function of intensity, pressure, wave length and temperature.

2. The quantum yield of carbon monoxide formation is small but increases with temperature. The same may be said for ethane.

3. The quantum yields for the main products of the reaction are nearly if not entirely independent of all the variables studied.

4. The data may be explained either by a free radical mechanism or by a primary decomposition into final products. Neither explanation can be said to be proved at the present time.

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