Photochemical Studies. XXIX. The Decomposition of Diethyl Ketone at Short Wave Lengths. A Comparison of Acetone, Ethyl Methyl Ketone and Diethyl Ketone Near 3000 Å.

BY VICTOR R. ELLS[1] AND W. ALBERT NOYES, JR.

The photochemical decompositions of acetone[2] and of ethyl methyl ketone[3] in the wave length region 1850–2000 Å. have been studied. The salient facts of these investigations may be summarized as follows.

(a) The quantum yield of carbon monoxide formation from acetone is about 0.50 at moderate pressures, increases with decreasing pressure, and attains a value of about 0.66 at a pressure of 0.2 mm. In the presence of foreign gases (CO_2, N_2, C_2H_6) this quantum yield is raised.

(b) The quantum yield of carbon monoxide formation from ethyl methyl ketone is about 0.70 at moderate pressures and becomes approximately 0.90 at low pressures.

(c) While for both compounds the ratio of carbon monoxide to hydrocarbons in the products is not far from 1:1, it was shown that diketones are produced upon irradiation of ethyl methyl ketone, both at these short wave lengths and in the near ultraviolet. The quantum yield expressed in terms of molecules of ethyl methyl ketone disappearing was shown to approach a value not far from unity at low pressures.

(d) The yield of methane from ethyl methyl ketone increases with temperature.

The photochemical decomposition of ethyl methyl ketone in the near ultraviolet has been investigated by Norrish and Appleyard,[4] who found the main reaction to give carbon monoxide and a mixture of ethane, propane, and butane. A small amount of decomposition to ethylene and acetaldehyde was also reported.

With ethyl methyl ketone two primary dissociations may be visualized

$$CH_3COC_2H_5 + h\nu = CH_3 + COC_2H_5 \quad (1)$$
$$CH_3COC_2H_5 + h\nu = C_2H_5 + COCH_3 \quad (2)$$
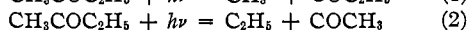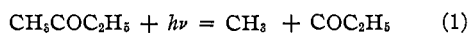
If the primary dissociations of simple ketones have quantum yields of unity, variations in yield are to be associated with the secondary reactions.

Since diethyl ketone can only give propionyl

radicals upon rupture of a single carbon–carbon bond adjacent to the carbonyl group, the behavior of this substance upon irradiation may furnish information concerning such radicals.

As shown by Matheson and Zabor,[5] the major portions of the fluorescences of diethyl ketone and of propionaldehyde are identical when excited by near ultraviolet radiation. Thus bipropionyl is probably one of the decomposition products in this region. Unfortunately, no satisfactory method of analyzing for small amounts of this diketone is now available so that quantum yields in the present article are merely those of carbon monoxide formation.

Experimental Procedure and Results

The diethyl ketone (Eastman Kodak Co.) was fractionally distilled several times, both at atmospheric pressure and at reduced pressure. Vapor pressures of this substance have been measured by Rintelen, Saylor and Gross[6] at 10, 30, and 50°, the values being 16.9, 46.1, and 117 mm., respectively. The maximum pressure attainable in the present work (at 27°) is about 38 mm.

The light source has been described,[2] and the method of gas analysis was essentially that of Manning,[7] which has been used with the other ketones.[2,3]

Liquid nitrogen was used first as a refrigerant, the only uncondensed gaseous product being carbon monoxide together with traces of ethane and ethylene. Ethane, butane, and ethylene were pumped off from pentane mush at a temperature between −150 and −155°. A slight hydrocarbon deficiency is again observed in spite of all precautions, indicating that such substances are soluble in the ketone and are difficult to remove.

The hydrogen bromide actinometer was used for measuring the number of quanta absorbed.

Table I shows gas analyses for four runs, two in which radiation from the full aluminum spark was used and two in which the region 1850–2000 Å. obtained through focal isolation was alone present.

(1) Fellow, during 1938–1939, of the Sherman Clarke Fund in Research Chemistry, The University of Rochester.

(2) Howe and Noyes, THIS JOURNAL, **58**, 1404 (1936).

(3) Ells and Noyes, *ibid.*, **60**, 2031 (1938).

(4) Norrish and Appleyard, *J. Chem. Soc.*, 874 (1934).

(5) Matheson and Zabor, *J. Chem. Phys.*, **7**, 536 (1939).

(6) Rintelen, Saylor and Gross, THIS JOURNAL, **59**, 1129 (1937).

(7) Manning, *ibid.*, **56**, 2589 (1934).

TABLE I

ANALYSES FOR HYDROCARBONS AND CARBON MONOXIDE

Pressure $(C_2H_5)_2CO$, mm.	31	28	35	35
Total hydrocarbons, mm.	0.0048	0.0043	0.0236	0.0121
C_4H_{10}, mm.	.0038	.0027	.0161	.0081
C_2H_6, mm.	.0005	.0008	.0038	.0022
C_2H_4, mm.	.0005	.0008	.0037	.0018
CO. mm.	.0045	.0039	.0217	.0108
$CO/[C_4H_{10} + \frac{1}{2}(C_2H_6 + C_2H_4)]$	1.05	1.11	1.09	1.07
% C_2H_5 giving C_4H_{10}	88	77	81	80
Conditions	1850–2000 Å.		Full spark	

From the data in Table I it is evident that most of the ethyl radicals combine to form butane although about 20% disproportionate to give ethane and ethylene. The excess of carbon monoxide is not definite evidence against the formation of bipropionyl because of the difficulty in pumping off the hydrocarbons completely.

Table II shows data for the quantum yield of carbon monoxide formation from diethyl ketone in the wave length region 1850–2000 Å. All runs were made at room temperature (25 ± 2°).

TABLE II

QUANTUM YIELDS OF CARBON MONOXIDE FROM DIETHYL KETONE (1850–2000 Å.)

Press. $(C_2H_5)_2$-CO, mm.	Time, min.	Intensity (arbitrary units)	Moles CO × 10⁵	Moles H_2 × 10⁵ (HBr actin-ometer)	Quantum yield of CO forma-tion
38	90	35.7	0.01254	0.01534	0.82
36	90	35.3	.00827	.00948	.87
31	120	35.2	.01283	.01340	.96
28	65	37.2	.00570	.00667	.85
22	120	34.3	.01112	.01283	.87
22	30	37.2	.00342	.00389	.88
17	40	38.0	.00228	.00258	.88
6	60	36.9	.00513	.00561	.91
4	60	36.6	.00371	.00389	.95

The figures in the fifth column are corrected for the thermal decomposition of hydrogen bromide and for the transmission of the windows. When multiplied by Avogadro's number these figures would give the number of quanta absorbed.

There seems to be a slight tendency for quantum yields to increase with decreasing pressure. The results scatter so much that an extrapolation has little meaning, but a value of unity at zero pressure would be compatible with the data. At comparable pressures the quantum yield of carbon monoxide formation is definitely higher for diethyl ketone than for ethyl methyl ketone[3] and for acetone.[2] Table III shows a comparison at even pressures of the values for the three ketones.

Since quantum yields of carbon monoxide for-

TABLE III

COMPARISON OF QUANTUM YIELDS OF CARBON MONOXIDE FORMATION AT SHORT WAVE LENGTHS FOR ACETONE, ETHYL METHYL KETONE AND DIETHYL KETONE 25 ± 2°

Pressure, mm.	$(CH_3)_2CO$	$CH_3COC_2H_5$	$(C_2H_5)_2CO$
20	0.52	0.76	0.88
8	.56	.78	.90
4	.59	.78	.95
1	.62	.82	(.98)
0.3	.64	.86	(.99)

Values in parentheses are obtained by rough graphical extrapolation.

mation increase with complexity of ketones in the region 1850–2000 Å. and since the quantum yield of carbon monoxide formation from acetone is considerably higher than in the near ultraviolet, it was deemed interesting to make a comparison of the ketones at the longer wave lengths.

An aluminum spark was used in conjunction with a red-purple corex filter for this comparison. The main lines absorbed by the ketones lie between 3050 and 3100 Å., but the radiation was not strictly monochromatic. At the low pressures used longer wave lengths would not be appreciably absorbed. The fractions of the incident radiations absorbed by the various ketones were determined with the aid of a photoelectric cell and proved to be nearly the same. While too great stress cannot be placed on absolute values, relative values are of interest in the present discussion.

The quantum yields given in Table IV are based on an assumed value of 0.095 ± 0.01 for that of carbon monoxide production from acetone at 25°.[8]

Based on the assumed value of 0.095 for acetone, the average quantum yield of carbon monoxide formation from ethyl methyl ketone is 0.11 and that from diethyl ketone is 0.97. Therefore, while the yields of the first two are low and nearly the same at 3000 Å., that of the latter is about the same at long as at short wave lengths.

(8) This figure is an average of a large number of runs made by one of us (W. A. N., Jr.) during 1931 using an absolute method with a thermopile calibrated by a standard light source. It agrees well with values which will be published in the near future from this Laboratory. The quantum yields obtained by Damon and Daniels [THIS JOURNAL, **55**, 2363 (1933)] and by Norrish, Crone, and Saltmarsh [J. Chem. Soc., 1456 (1934)] are slightly higher but were obtained at higher temperatures. Since Leermakers [THIS JOURNAL, **56**, 1899 (1934)] has shown the yield to be unity at 163°, the value cited at 25° is a reasonable one in comparison with the others. At 3130 Å. and a temperature of 56° Damon and Daniels found a considerable falling off of yield with pressure. In the unpublished work just cited little change with pressure between 5 and 16 cm. could be found. Pressures in Table IV are below 5 cm. so that some doubt exists concerning absolute values.

TABLE IV

COMPARISON OF QUANTUM YIELDS OF CARBON MONOXIDE
FORMATION FROM THREE KETONES NEAR 3000 Å.

Assuming yields to be 0.095 for acetone. The values at 10 mm. pressure are least accurate because of the small amount of absorption.

Ketone	Pressure, mm.	Press. CO formed ($V = 531$ cc.), mm.	Quantum yield of CO formation
CH_3COCH_3	10	0.0007	(0.095)
$CH_3COC_2H_5$	10	.0006	.082
$C_2H_5COC_2H_5$	10	.0049	.67
CH_3COCH_3	10	.0006	(.095)
$CH_3COC_2H_5$	10	.0007	.11
$C_2H_5COC_2H_5$	10	.0062[a]	.98
CH_3COCH_3	21	.0009	(.095)
$CH_3COC_2H_5$	21	.0011	.12
$C_2H_5COC_2H_5$	21	.0092	.97
CH_3COCH_3	36	.0013	(.095)
$CH_3COC_2H_5$	36	.0016	.12
$C_2H_5COC_2H_5$	36	.0142[b]	1.04

[a] Pressure of butane + ethane + ethylene in this experiment is 0.0060. 0.93 of the ethyl groups form butane, and the remainder disproportionate to ethane and ethylene. [b] Total pressure of hydrocarbons 0.0136 mm. in this experiment.

Discussion of Results

The details of the mechanism of photochemical acetone decomposition in the near and far ultraviolet have not yet been elucidated completely. Since the quantum yield of carbon monoxide formation is appreciably greater at 1850–2000 Å. than at longer wave lengths, it is evident either that the acetyl radical separates with enough energy to make it inherently unstable or that secondary reactions leading to carbon monoxide formation are, for some reason, more probable under the conditions under which the short wave experiments were carried out.

From a variety of sources it is quite certain that the quantum yield of the primary process
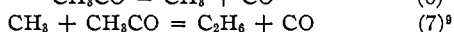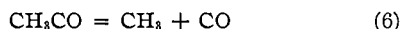
$$CH_3COCH_3 + h\nu = CH_3 + COCH_3 \qquad (3)$$

is very close to unity in the near ultraviolet.[9] The low yield of carbon monoxide formation may be due to the reactions

$$CH_3CO + CH_3CO = (CH_3CO)_2 \qquad (4)$$
and
$$CH_3CO + CH_3 = CH_3COCH_3 \qquad (5)$$
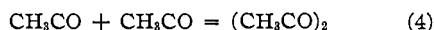
The mechanism by which carbon monoxide is produced is uncertain, but two possibilities suggest themselves

$$CH_3CO = CH_3 + CO \qquad (6)$$
$$CH_3 + CH_3CO = C_2H_6 + CO \qquad (7)[9]$$

Gorin believes that (6) has too high an activation

(9) See Gorin, *J. Chem. Phys.*, **7**, 256 (1939).

energy to be important at ordinary temperatures and ascribes carbon monoxide production to (7). While no adequate evidence for or against this choice is available as regards the work in the near ultraviolet, a comparison of the yield at 1850–2000 Å. with that at longer wave lengths makes it appear probable that (6) is important in the former region. It should be noted that (3) followed by (6) would be difficult to distinguish clearly from a primary dissociation into two methyls and carbon monoxide.

If the energy required to produce reaction (3) is assumed to be 70 kcal., a wave length of 3130 Å. provides an excess of 21 kcal. per gram molecule. If the excess appears merely as translational energy, the acetyl radicals would possess 5.5 kcal. of energy per gram molecule in that form. Since, however, they have more degrees of freedom than methyl radicals, they might be expected to retain more than half if all were in the form of vibrational energy. Nevertheless, sufficient energy to cause dissociation would scarcely be available if the activation energy (17 kcal.) assumed by Gorin for (6) is correct. At 2536 Å. the acetyl radicals would acquire 10 kcal. if the energy were all translational. This would still be inadequate to evoke (6) except in a few collisions where thermal energy could supply the deficiency. At 1900 Å., however, 20 kcal. would be given to the acetyl radical as kinetic energy. This could cause dissociation at the first impact by reaction (6). The high quantum yield of CO formation at short wave lengths can be explained in this way. In ethyl methyl ketone, the acetyl radical would acquire more kinetic energy of translation than from acetone, assuming no energy in vibrational degrees of freedom. No account is taken of electronic excitation in these simple calculations.

A quantum yield expression derived from (3), (4), (5), (7), and (8)

$$CH_3 + CH_3 = C_2H_6 \qquad (8)$$

shows no variation with either intensity or with pressure as long as all reactions occur in the homogeneous gas phase and third bodies are unimportant. The inclusion of (6) would mean necessarily that the quantum yield of carbon monoxide formation would increase at low intensities although the formal expression is very complex. While no very good evidence exists on this point at present, such as is available favors this sort of variation with intensity.[10]

(10) Damon and Daniels, THIS JOURNAL, **55**, 2363 (1933).

At short wave lengths the main portion of carbon monoxide must be formed by a spontaneous dissociation of the acetyl radical. All combination reactions of free radicals which would reduce carbon monoxide formation must be relatively unimportant. Only in this way can the lack of intensity effect on the yield be accounted for unless one wishes to admit a peculiar enhancement of the rate of (7) for at present unknown reasons.

When attention is turned to ethyl methyl ketone, the situation becomes very difficult to understand unless some spontaneous dissociation of the radicals CH_3CO and C_2H_5CO is allowed. It is not very satisfactory, although it may prove necessary to postulate nearly all possible types of primary dissociation of this molecule,[9] including a production of propane and carbon monoxide in one step.

In the decomposition of diethyl ketone, either in the near or in the far ultraviolet, the quantum yield of carbon monoxide formation is not far from unity. If the primary process is

$$(C_2H_5)_2CO + h\nu = C_2H_5 + C_2H_5CO \qquad (9)$$

the propionyl radical must either be very unstable, or it must undergo a very probable reaction analogous to (7). The recombination reactions

$$C_2H_5CO + C_2H_5 = C_2H_5COC_2H_5 \qquad (10)$$
$$C_2H_5CO + C_2H_5CO = (C_2H_5CO)_2 \qquad (11)$$
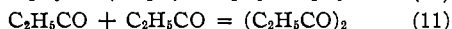
cannot be important. Some evidence for a slight occurrence of (11) is found from a study of the fluorescence of diethyl ketone.[5]

Without considering for the moment the mechanism by which carbon monoxide may be produced from propionyl radicals, let us assume merely that 90% of such radicals yield carbon monoxide. The acetyl radical may be expected to give carbon monoxide (in the near ultraviolet) not more than one-tenth of the time. Therefore if primary processes (1) and (2) are equally probable, the quantum yield of carbon monoxide production from ethyl methyl ketone should be 0.50 in the near ultraviolet. The data in Table IV show that this is not the case, the actual yield being little greater than for acetone.

It seems necessary to conclude, therefore, that primary process (2) predominates.[11] If one as-

sumes that the low yield of carbon monoxide from ethyl methyl ketone is due to the recombination

$$C_2H_5 + COCH_3 = C_2H_5COCH_3 \qquad (12)$$

and that 0.1 of the acetyl radicals and 0.9 of the propionyl radicals yield carbon monoxide, it can be shown that 0.98 of the primary dissociation goes by (2) and 0.02 by (1). A slight combination between methyl and acetyl radicals would alter these figures somewhat, and acetone would be predicted to appear among the products. The amount of diethyl ketone produced should be negligible, but, on the other hand, biacetyl should result from combinations between acetyl radicals. Since the main part of the fluorescence of ethyl methyl ketone is identical with those of acetaldehyde, acetone, and biacetyl, the occurrence of biacetyl among the products is probable.

The fact that approximately equal quantities of ethane, propane, and butane are produced both in the near and far ultraviolet is difficult to explain with any distribution of methyl and ethyl radicals and must be due to peculiarities in the rates of production of these gases from free radicals.[3] With the above mechanism approximately equal numbers of the two free radicals should form hydrocarbons.

In the far ultraviolet if 0.55 of the acetyl radicals yield carbon monoxide, 0.9 of the propionyl radicals yield carbon monoxide, and the over-all yield of carbon monoxide is 0.80, it can be shown that primary process (1) is slightly more probable than (2). However, variations in the ratio are quite sensitive to the quantum yield figures. Since an amount of energy considerably in excess of that necessary to cause dissociation is absorbed at these wave lengths, slight differences in bond strength might be expected to make little difference in the nature of the dissociation.

The fact that butane is the principal hydrocarbon resulting from the photochemical decomposition of diethyl ketone is not surprising. The extents to which ethyl radicals combine to form butane and disproportionate to ethane and ethylene have not been determined satisfactorily. Perhaps one or the other or both of these reactions occurs on the walls. The results of Meinert[12] on the thermal decomposition of tetraethyllead indicate a high probability of butane formation. The 1:1 ratio of ethane to ethylene is evidence, although not proof, against other reactions intervening in the production of ethane and ethylene.

(11) Professor G. B. Kistiakowsky suggested at a symposium held at Stanford University, August 8–11, 1938, that much of the work on photochemistry of ketones could be explained by assuming that the molecules usually split on the side of the carbonyl group toward the heaviest radical.

(12) Meinert, THIS JOURNAL, **55**, 979 (1933).

Summary

1. The quantum yield of carbon monoxide formation from diethyl ketone in the wave length region 1850–2000 Å. is quite high and seems to approach unity as the pressure is lowered.

2. With an assumed quantum yield of 0.095 at 3000 Å. for carbon monoxide formation from acetone it has been shown that the yield from ethyl methyl ketone is only slightly higher and that that of diethyl ketone is about one.

3. These facts indicate either a high intrinsic instability of propionyl radicals or very probable reactions involving them which lead to carbon monoxide.

4. Ethyl methyl ketone probably dissociates almost but not quite solely to give ethyl radicals in the near ultraviolet. At short wave lengths methyl and ethyl radicals are produced in nearly equal amounts from the primary process.

5. Most of the ethyl radicals form butane, but a small fraction yield ethane and ethylene.

The Palladium–Deuterium Equilibrium

BY LOUIS J. GILLESPIE AND WILLIAM RICHARD DOWNS

The purpose of this investigation has been to study the absorption of deuterium by palladium black in the region of temperature and pressure in which hydrogen and palladium have been found by Brüning and Sieverts[1] and by Gillespie and Galstaun[2] to exhibit a critical solution temperature, and inclusive of the region at 200° and above in which hydrogen and palladium exhibit a tendency toward compound formation—in short, to obtain part of the phase diagram for deuterium and palladium analogous to that of Gillespie and Galstaun for hydrogen and palladium.

Sieverts and Zapf[3] studied the solubility of hydrogen and of deuterium in a palladium wire. The ratio of the solubility of deuterium to that of hydrogen was 0.67 at 300° and increased to 0.91 at 1000°.

Sieverts and Danz[4] studied the absorption of deuterium by palladium black from 20 to 350° at various low pressures (less than 2 atm.). Isotherms at 80 and 100° gave evidence of two solid phases, but in all cases, even for the corresponding curves for hydrogen, there was considerable hysteresis. Sieverts and Danz[5] have also studied the electrical resistance and magnetic susceptibility of palladium wire charged with deuterium.

Since the early work of Oxley[6] the magnetic susceptibility of palladium charged with hydrogen has also been studied by Aharoni and

Simon,[7] Svensson,[8] and Michel and Gallissot.[9] The latter have also studied the variations of the lattice parameter, the Brinell hardness and the electrical resistance as hydrogen is added to the metal.

There are recent X-ray studies of the system palladium–hydrogen by Kruger and Gehm[10] and by Owen and Jones.[11] The latter, as well as Michel and Gallissot, found in agreement with the early experience of Wolf[12] that simple degassing of palladium that has been well charged with hydrogen—to the formation of the second (beta) solid solution—does not entirely restore the original physical constants of the palladium, but that high temperature annealing (e. g., 450° for one-half hour[11]) is necessary and sufficient.

This finding is of two-fold interest in connection with the equilibrium of either hydrogen or deuterium with palladium. In the first place, one need not expect the whole of an isotherm containing a horizontal portion to be reversible, since the palladium would appear not to be the same for the first rising portion when traced upward from zero concentration as when later traced downward after formation of the beta phase and its subsequent decomposition. This effect seems, however, to be rather theoretical than actual. In the second place, one might expect that any reluctance to form the beta phase, if once over-

(1) Brüning and Sieverts, Z. physik. Chem., 163A, 409 (1933).
(2) Gillespie and Galstaun, THIS JOURNAL, 58, 2565 (1936).
(3) Sieverts and Zapf, Z. physik. Chem., 174A, 359 (1935).
(4) Sieverts and Danz, ibid., 38B, 46 (1937).
(5) Sieverts and Danz, ibid., 38B, 61 (1937).
(6) Oxley, Proc. Roy. Soc. (London), 101A, 264 (1922).

(7) Aharoni and Simon, Z. physik. Chem., 4B, 175 (1929).
(8) Svensson, Ann. Physik, 18, 299 (1933).
(9) Michel and Gallissot, Compt. rend., 208, 434 (1939).
(10) Kruger and Gehm, Ann. Physik, 16, 174 (1933).
(11) Owen and Jones, Proc. Phys. Soc., 49, 587, 603 (1937).
(12) Wolf, Z. physik. Chem., 87, 588 (1914).