A similar run using 2.25 moles of acid chloride was also completed and the material from both reactions boiling above the secondary carbinol was refractionated to give 8 fractions, 61.1 g., b. p. 90° (5 mm.), n^{20}_{D} 1.4392–1.4359. Refractionation of these gave 8 fractions, 39.7 g., b. p. 90° (5 mm.), n^{20}_{D} 1.4367–1.4339, which represented a 5% yield of *t*-butylneopentylcarbinyl *t*-butylacetate. The refractive index gradually approached the correct index for the synthetic ester, n^{20}_{D} 1.4320. The boiling point was correct for the ester. The mol. wt. found from the depression of the f. p. of benzene is 250; calcd. 256.

The fractions of the two preparations boiling in the range of 79–168° (732 mm.), were combined and refractionated to give 2 fractions, wt. 6.9 g., b. p. 139–143°, n^{20}_{D} 1.4150–1.4179. These were identified as neopentylcarbinol by means of the α-naphthylurethan, m. p. 82–83°, which gave no depression with α-naphthylurethan of known neopentylcarbinol. The yield of this reduction product was thus 1%.

An addition of 0.65 mole of *t*-butylacetyl chloride to 1.5 moles of *t*-butylmagnesium chloride produced the secondary carbinol in 76% yield with no evidence for the formation of *t*-butylneopentylcarbinyl *t*-butylacetate.

Addition of *t*-Butylmagnesium Chloride to *t*-Butylacetyl Chloride.—To a solution of 128 g. (0.95 mole) of *t*-butylacetyl chloride in 1300 cc. of ether was added one mole of *t*-butylmagnesium chloride in a liter of ether over a period of thirty-six hours. The addition complex was decomposed with ice, extracted with ether, and the product fractionated, after removal of solvent, to give: 1, 2, 54.8 g., b. p. 33–110° (728 mm.), n^{20}_{D} 1.3520–1.3640; 3–6, 7.8 g., 110–158°, 1.4042–1.4125; 7–9, 18.9 g., 158–161°, 1.4135–1.4150; 10–12, 75.4 g., 161°, 1.4158–1.4160; 13–14, 15.9 g., 161–164°, 1.4167–1.4175; residue, 39.2 g. Fractions 10–12 represent a 51% yield of *t*-butyl neopentyl ketone, which did not form a semicarbazone or oxime and yielded a 2,4-dinitrophenylhydrazone with great difficulty, m. p. 123.5–124.5°.

The residue of this fractionation was combined with that of a 0.5 mole run to give 6 fractions of pure *t*-butylneopentylcarbinyl *t*-butylacetate, wt. 33 g. (17% yield), b. p. 90° (5 mm.), n^{20}_{D} 1.4320, d^{20}_{4} 0.8553. Molecular refraction; calcd. 77.74, found 77.73. *Anal.* Calcd. for $C_{16}H_{32}O_2$: C, 75.0; H, 12.5. Found: C, 75.6; H, 12.6.

Treatment of 19.8 g. of the pure ester with 12 g. of potassium hydroxide in 60 cc. of absolute methyl alcohol at reflux temperature for seventy-one hours gave no evidence of saponification. Treatment of 16.7 g. of the ester with 20 g. of potassium hydroxide in 125 cc. of 95% ethyl alcohol in a sealed tube at 90–100° for fifty-six hours likewise gave no evidence of saponification.

Preparation of *t*-Butylneopentylcarbinyl *t*-Butylacetate.—The addition of 53 g. (0.39 mole) of *t*-butylacetyl chloride to 55.3 g. (0.35 mole) of *t*-butylneopentylcarbinol, m. p. 50–51°, gave a slight evolution of heat. The reaction mixture was refluxed for two hours, cooled, washed with 10% sodium carbonate solution, dried with anhydrous potassium carbonate and fractionated to give: 1–5, 22.2 g., b. p. 30–94° (5–7 mm.), n^{20}_{D} 1.4188–1.4260; 6–8, 16.5 g., 93° (7 mm.), 1.4312–1.4316; 9–12, 36.0 g., 93° (7 mm.), 1.4318–1.4320; 13, 5.7 g., 93° (7 mm.), 1.4311; residue, 1.6 g. Fractions 6–13 represent 65% yield of the ester. A density determination on fraction 10, n^{20}_{D} 1.4320, indicated d^{20}_{4} 0.8549. Treatment of 10 g. of the synthetic ester with 20 g. of potassium hydroxide in 120 cc. of 95% ethyl alcohol gave no indication of saponification after refluxing the mixture for seventy-two hours.

Summary

1. A study has been made of the normal addition and reduction products formed by the addition of *t*-butylacetyl chloride to *t*-butylmagnesium chloride and of those formed by the reverse addition.

2. The synthesis and physical constants of *t*-butylneopentylcarbinyl *t*-butylacetate have been described.

STATE COLLEGE, PENNA. RECEIVED JUNE 4, 1938

[CONTRIBUTION FROM THE METCALF CHEMICAL LABORATORY OF BROWN UNIVERSITY]

Photochemical Studies. XXVIII. The Photochemical Decomposition of Ethyl Methyl Ketone by Wave Lengths from 1850–2000 Å.

BY VICTOR R. ELLS AND W. ALBERT NOYES, JR.

Ethyl methyl ketone, in common with other ketones, absorbs in the near ultraviolet, the approximate limits being 2400 and 3200 Å. No discrete structure could be found in this region,[1] although fluorescence may be excited, at least by the 3130 Å. line of mercury. However, recent work[2] on the fluorescence of acetone has raised the question as to whether the ketones or some of their decomposition products are mainly responsible for the emission of fluorescent radiation.

The photochemical decomposition of ethyl methyl ketone in the near ultraviolet has been investigated by Norrish and Appleyard.[3] The products of the reaction were found to be carbon monoxide and approximately equal amounts of ethane, propane and butane, together with small amounts of ethylene and acetaldehyde. In the

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(1) Duncan, Ells and Noyes, THIS JOURNAL, **58**, 1454 (1936).

(2) Matheson and Noyes, *ibid.*, **60**, 1857 (1938).

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

analogous decomposition of acetone at room temperature, biacetyl has been shown to be one of the main products.[4]

The second region of absorption in ketones occurs just below 2000 Å. and may be investigated also with the aid of quartz apparatus. At these wave lengths acetone gave approximately equal amounts of hydrocarbon (ethane) and carbon monoxide,[5] indicating thereby that little or no biacetyl is formed. However, the quantum yield for the decomposition did not approach unity, apparently, as the pressure was lowered, thus leading to some difficulties in the theoretical interpretation of the results.

The present work was undertaken with the object of ascertaining whether ethyl methyl ketone behaves in a manner analogous to acetone in the region of 1850 to 2000 Å. or whether the quantum yield is higher. The entire question of the adiabatic transfer of polyatomic molecules between energy states rests on a very insecure theoretical foundation and the introduction of such an idea[6] was made only because of the apparent difficulty in accounting by more rational means for the fate of all of the absorbed energy.

As will be seen it is not necessary, for ethyl methyl ketone, to use unorthodox ideas for the explanation of the experimental facts, at least in the wave length region studied.

Experimental Procedure and Results

(a) **The Determination of Diketones among the Reaction Products in the Near Ultraviolet.**—Since it is quite important to know all of the reaction products in order to arrive at a proper estimate of the quantum yield, it was decided first to ascertain whether diketones are produced upon irradiation of ethyl methyl ketone in the near ultraviolet region.

Reactions were carried out in a Pyrex cell with plane window using as a light source a capillary mercury arc.[7] The wave lengths were greater than 3000 Å. and the absorption was due almost entirely to the group of lines near 3130 Å.

The ethyl methyl ketone was synthesized by the acetoacetic ester synthesis. Ethyl acetoacetate was added to the proper amount of sodium metal dissolved in ethyl alcohol to form the sodium compound of the enol form. Methyl iodide was added and the mixture refluxed for several hours until it no longer gave an alkaline reaction. The alcohol was distilled off, water added and the ethyl methylacetoacetate extracted with diethyl ether. After purification by fractional distillation, the ethyl methylacetoacetate was hydrolyzed with 10% sodium hydroxide and the ethyl methyl ketone distilled off. In addition to fractional distillation, the ethyl methyl ketone was purified by formation of the bisulfite compound which was decomposed by potassium carbonate to reform the ketone. Fused potassium carbonate was used as the final drying agent. The boiling point of the final material was 79.4 ± 0.2°.

The ethyl methyl ketone was kept flowing through the reaction cell by immersing traps in water at different temperatures. After irradiation for a period of sixty to one hundred hours, liquid air was placed on one of the traps and the non-condensable gases collected by means of a Toepler pump, after which they were analyzed for carbon monoxide by the method of Blacet and Leighton.[8]

The condensed liquids were removed from the system and treated with hydroxylamine hydrochloride, nickel chloride and ammonium hydroxide solutions to quantitatively precipitate the diketones as nickel glyoxime salts. The precipitates were filtered through Gooch crucibles and weighed. Although a method has been developed by Johlin[9] for separating some of the possible salts, the small amount of precipitate (1–3 mg.) rendered this impracticable, so that an average molecular weight of 316.9 was taken.

Four runs were made showing that the following percentages of carbon monoxide appeared as diketones among the reaction products: 11.7, 9.9, 11.3, 10.6; average 10.9. It is apparent, therefore, that diketones are formed upon irradiation of ethyl methyl ketone in the near ultraviolet and this fact must be taken into account in obtaining a final theory of the mechanism of the reaction.

(b) **The Determination of the Quantum Yield at 1850–2000 Å.**—The light source has been described[5] and consisted of a spark between rotating aluminum disks. The group of lines from 1855 to 1990 Å. was separated by focal isolation. In this region ethyl methyl ketone shows several bands[1] and a weak continuous absorption.

The method of gas analysis used for the products was essentially that described by Manning[10] and used in the work on acetone.[5] After irradiation, the ethyl methyl ketone and products were, as far as possible, condensed with liquid air and the residual gases (carbon monoxide, ethane and methane, if present) were pumped off with a Toepler pump and measured with a McLeod gage. Prolonged pumping and several evaporations and recondensations were necessary to effect removal of the ethane. The analysis of this fraction was carried out exactly as described.[10] No ethylene was found in these gases, indicating that the Type II decomposition of ethyl methyl ketone described by Norrish and Appleyard[3] does not seem to be very important in this wave length region.

A second fraction of reaction products was next removed by replacing the liquid air by a solid–liquid pentane mixture at about −155°. This fraction would contain propane and butane as well as any acetaldehyde and carbon dioxide which might have been formed. This fraction was burned with oxygen using the hot platinum wire as previously described.[10]

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[4] Barak and Style, *Nature*, **135**, 307 (1935); Spence and Wild, *ibid.*, **138**, 206 (1936); *J. Chem. Soc.*, 352 (1937).

[5] Howe and Noyes, THIS JOURNAL, **58**, 1404 (1936).

[6] Norrish, Crone and Saltmarsh, *J. Chem. Soc.*, 1456 (1934).

[7] Heidt and Daniels, THIS JOURNAL, **54**, 2381, 2384 (1932).

[8] Blacet and Leightan, *Ind. Eng. Chem.*, *Anal. Ed.*, **3**, 266 (1931); Blacet, Leighton and McDonald, *ibid.*, **5**, 272 (1933).

[9] Johlin, THIS JOURNAL, **37**, 892 (1915).

[10] Manning, *ibid.*, **56**, 2589 (1934).

In all cases an excess of carbon monoxide was found, indicating superficially, as with acetone,[5] that diketones were not formed. However, it has been emphasized by Norrish and his co-workers[6] that the hydrocarbons are quite soluble in the condensed ketones and that some difficulty is encountered in effecting their removal.

To further test the possibility of diketone formation, the spectrum of biacetyl was photographed in the far ultraviolet.[11] An intense band at 57,295 cm.$^{-1}$, which is well removed from any bands of ethyl methyl ketone,[1] could be used for the identification of biacetyl. Other bands also furnished confirmatory evidence for the formation of this compound. A series of photographs was made with known pressures of biacetyl and a comparison of the spectra of the reaction products, from which carbon monoxide and ethane had been removed, with these standards permitted a very rough estimate to be made of the amount of biacetyl produced. No estimate of the amounts of the other possible diketones could be made, so that the three were assumed to be present in equal amounts. Moreover, some diketones would be formed during the photographing of the spectrum so that no great accuracy is claimed for the amount of diketones formed. One band at 58,086 cm.$^{-1}$ which appeared on some of the spectra may have been due to one of the other diketones.

The hydrogen bromide actinometer was used, as previously,[5] for the determination of the number of quanta absorbed. Runs made with the purpose of obtaining proof for the existence of biacetyl were made in an all quartz cell and the results agreed with those obtained in the cell with windows attached by wax.

Table I shows the analysis of the gases formed during reaction.

TABLE I

COMPOSITION OF REACTION PRODUCTS

Ketone pressure, mm.	Carbon monoxide (mm. in anal. app.)	Hydrocarbons, mm.	% Carbon monoxide	Ethane, mm.	Propane, mm.	Butane, mm.
70	0.0222	0.0197	53.0	0.0062	0.0066	0.0069
62	.0140	.0089	61.1	.0026	.0034	.0029
58	.0129	.0099	56.6	.0036	.0035	.0028
25	.0182	.0157	54.0	.0056	.0054	.0047
14	.0224	.0227	49.7	.0079	.0071	.0077
4	.0114	.0099	53.5	.0032	.0035	.0032
11	.0176	.0135	56.6	.0049	.0045	.0041

From the data in Table I it is seen that the average ratio ethane:propane:butane is 1:1.03:0.95, so that the relative amounts of these hydrocarbons agree very closely with those reported by Norrish and Appleyard[3] in the near ultraviolet.

Table II presents data on the number of molecules of carbon monoxide produced per quantum absorbed by ethyl methyl ketone.

In order to estimate how much biacetyl was formed, the spectrum of this substance was photographed in a 15-cm. tube at pressures which were estimated on a McLeod gage. As little as 0.0001 to 0.0002 mm. was sufficient to cause the 57295 cm.$^{-1}$ band to be recognizable.

After irradiation of ethyl methyl ketone, the liquids were condensed with liquid air and the carbon monoxide and ethane were pumped off. The trap, which was fitted with a small bulb which could be broken by a magnetic hammer, was sealed off and attached to the cell in front of the spectrograph. The trap was immersed in dry ice–ether mixtures during the photographing of the spectrum. The vapor pressure of biacetyl is about 0.01 mm. at $-70°$ and about 0.004 mm. at $-77°$.

The volume of the cell used for photographing the spectrum was about 0.13 of the volume in which the gases were measured in the quantum yield determinations. If the three diketones are formed in equal amounts, multiplying the number of molecules of biacetyl by six will give the number of molecules of ethyl methyl ketone which have disappeared during irradiation due to diketone formation. Multiplication of the approximate pressure of biacetyl in the absorption cell by 0.77 gives the pressure of ethyl methyl ketone which would have disappeared in the larger volume.

Table III gives rough estimates of the extent of the diketone reaction in four runs.

The order of magnitude of the fraction of the reaction which leads to diketone formation seems to be the same as in the near ultraviolet, but the data are too inaccurate to permit a definite statement on this point to have much meaning.

It should be mentioned in passing that similar experiments were performed on acetone after the conclusion of this work to ascertain whether biacetyl was formed in sufficient quantity to make a correction necessary on the previous work.[5] No biacetyl could be detected in this case, but this matter is worthy of a more thorough investigation.

Since biacetyl is formed to a considerably less extent from acetone in the near ultraviolet as the temperature is increased it was decided to make quantum yield determinations at higher temperatures. Moreover, Winkler[12] studied the photochemical decomposition of acetone from 60 to 400°, at wave lengths 2200 to 3200 Å. and found methane and ketene among the products, the ketene being detected by effects observed by Ross and Kistiakowsky.[13] The quantum yield which was 0.3 at 60° increased to 1 at 160°.

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(11) Ells, THIS JOURNAL, **60**, 1864 (1938).

(12) Winkler, *Trans. Faraday Soc.*, **31**, 761 (1935).

(13) Ross and Kistiakowsky, THIS JOURNAL, **56**, 1112 (1934).

TABLE II

NUMBER OF MOLECULES OF CARBON MONOXIDE PRODUCED PER QUANTUM ABSORBED

Run	Ketone press., mm.	Molecules CO $\times 10^{-17}$	Intensity (arbitrary units)	Incident quanta $\times 10^{-17}$	Fraction absorbed	Absorption coeff.[a] k	Quantum yield
27	90	0.605	18.2	0.94	0.92	0.028	0.70
24	52	.753	20.0	1.20	.77	.029	.81
20	30	1.113	15.9	1.86	.79	.053	.76
23	25	1.113	19.2	1.72	.83	.072	.77
21	24	0.589	18.4	1.06	.79	.065	.71
29	24	1.064	19.1	1.83	.77	.061	.76
18	22	1.178	23.2	2.66	.57	.039	.77
22	16.5	1.113	18.0	1.91	.77	.088	.76
14	14	4.388	20.4	6.66	.85	.135	.77
17	11	3.448	18.8	6.32	.72	.11	.76
19	8	1.636	18.3	2.97	.69	.15	.79
25	6	0.982	20.7	1.57	.82	.29	.76
31	5	1.505	19.6	2.50	.78	.30	.77
15	4	2.233	17.1	5.40	.58	.22	.71
26	1.75	0.605	20.2	1.30	.63	.63	.74
33	1.00	.654	17.9	1.71	.47	.63	.82
28	0.75	.392	17.6	1.60	.30	.47	.83
30	.73	.982	18.6	3.63	.31	.51	.87
32	.34	.245	18.8	2.55	.115	.60	.84
34	.09	.196	17.2	4.25	.052	.59	.88
35[b]	.017	.098	17.6	....	(.010)	(.60)	(1.2)
46[b]	.018	.196	17.8	....	(.010)	(.60)	(1.1)
36[c]	18	1.685	22.2	3.14	.71	....	0.75

[a] The absorption coefficient is calculated from the equation—kp (mm.) = $\ln_e$ (*fraction transmitted*). It is quite evident that Beer's law is not obeyed for the radiation used, thus indicating that more than one wave length is being absorbed. [b] The quantum yield in these runs is calculated using the same k (0.60) as found in Run 34. Since the fraction absorbed is thus probably too low, the quantum yields are probably too high. [c] This run was made in the all quartz cell referred to above.

TABLE III

EXTENT OF THE DIKETONE REACTION

Run	Ketone pressure, mm.	Estimated pressure biacetyl (abs. cell)	Press., CO, mm.	Equiv. press. of ethyl methyl ketone (in anal. app.)	Approx. quantum yield of diketone reaction
46	0.018	0.0001	0.0012	0.0001	0.06
45	13	.0020	.0250	.0016	.05
44	14	.0085	.0890	.0070	.06
47	43	.0012	.0080	.0009	.08

In the present work on ethyl methyl ketone runs were made from 100 to 200°. No thermal decomposition was found, but methane was formed photochemically. No method of testing for ketenes was practicable. Table IV presents the data.

TABLE IV

QUANTUM YIELD AT ELEVATED TEMPERATURE

Run	Ketone press., mm.	Temp., °C.	Quantum yield of CO formation	Fraction absorbed	Ratio CO/CH_4	Quantum yield of CH_4 formation
47	43	105–110	0.79	0.60	4.2	0.19
41	4.75	160–165	.79	.36	4.0	.20
42	45	160–165	.85	.74	2.2	.38
48	43	195–200	.71	.59	1.5	.47

The amount of methane seems to increase both with increasing temperature and with increasing pressure. In run 47 a spectroscopic test was made for biacetyl and only a trace was found. This might have been produced during the photographing of the spectrum.

Discussion

It is quite evident from the data in Tables II and III together that as the pressure is lowered the over-all quantum yield for the disappearance of ethyl methyl ketone in the wave length region 1850–2000 Å. approaches unity. The highest value observed experimentally is about 0.95 and this is well within the experimental error of 1.00.

At higher pressures the yield decreases, so that the average of runs conducted at pressures over 20 mm. is 0.83 (allowing 0.08 for the biacetyl reaction).

Since Beer's law is not obeyed, it is necessary to allow for at least two and probably more different types of absorption. Thus we may write down the following primary processes

$$I_1 \qquad K + h\nu = K_1 \tag{1}$$

$$I_2 \qquad K + h\nu = CH_3CO + C_2H_5 \tag{2}$$

$$I_3 \qquad K + h\nu = C_2H_5CO + CH_3 \tag{3}$$

where K represents a molecule of ethyl methyl ketone and K_1 an excited molecule. The active molecules may fluoresce, may dissociate or may be deactivated by collision. No fluorescence could be detected in the visible, in contradistinction to the behavior in the near ultraviolet.[1] With acetone, also,[5] no fluorescence excited by these wave lengths could be detected. Therefore we may write the following reactions for K_1:

$$\begin{array}{llr} k_1 & K_1 + K = K + K & (4) \\ k_2 & K_1 = CH_3CO + C_2H_5 & (5) \\ k_3 & K_1 = C_2H_5CO + CH_3 & (6) \end{array}$$

If, now, none of the free radicals recombine to give ethyl methyl ketone, we arrive at the following expression for the quantum yield of ketone decomposition

$$\Phi = \frac{1}{I_1 + I_2 + I_3}\left[I_2 + I_3 + \frac{I_1}{\frac{k_1(K)}{k_2 + k_3} + 1}\right] \qquad (7)$$

Since the relative values of I_1, I_2 and I_3 change with pressure, the quantitative application of equation (7) would have little meaning. It is evident, however, that it may be made to fit the data on quantum yields. According to this equation the yield should become one at zero pressure and this seems to be true. At higher pressures the variation of quantum yield will depend upon the relative magnitudes of the absorption coefficients for the three primary processes as well as on the magnitudes of k_1, k_2 and k_3. Little more can be said concerning the variation of over-all quantum yield from the data at room temperature.

There may be a slight tendency for the amount of biacetyl to increase with the pressure, the tendency of this substance to dissolve in the ethyl methyl ketone being a factor which might prevent the increase from becoming more noticeable. This could be explained easily on the basis of the higher optical absorption and consequently greater chance of reaction between free radicals.

If (1), (2) and (3) are the only primary processes (the simultaneous splitting off of both alkyl groups would not be impossible), the following equations must be considered

$$\begin{array}{lllr} CH_3CO & = CH_3 + CO & & (8) \\ C_2H_5CO & = C_2H_5 + CO & & (9) \\ CH_3CO & + CH_3CO & = (CH_3CO)_2 & (10) \\ CH_3CO & + C_2H_5CO & = CH_3COCOC_2H_5 & (11) \\ C_2H_5CO & + C_2H_5CO & = (C_2H_5CO)_2 & (12) \\ CH_3 & + CH_3 & = C_2H_6 & (13) \\ CH_3 & + C_2H_5 & = CH_3CH_2CH_3 & (14) \\ C_2H_5 & + C_2H_5 & = C_4H_{10} & (15) \end{array}$$

As the temperature is increased, methane could be formed by

$$CH_3 + CH_3COC_2H_5 = CH_4 + C_4H_7O \text{ (free radical)} \qquad (16)$$

Rice and Herzfeld[14] ascribe a heat of activation of 15,000 cal. to the analog of (16) in acetone. The free radical could split off an ethyl or a methyl group to give ketene or methyl ketene. For this reaction Rice and Herzfeld give an activation energy of 48,000 cal., so that it would become important only at high temperatures.

The fact that equal quantities of the hydrocarbons ethane, propane and butane have been found in this work as well as by Norrish and Appleyard[3] is quite interesting. Presumably these reactions occur through the formation of quasi-molecules which must be stabilized by collision with a third body. That a statistical equilibrium is not established is evident since there is not twice as much propane as of either of the others. The number of binary collisions for (13), (14) and (15) will be in the ratio 1.00:0.87:0.83. With equal concentrations of the free radicals, the same steric factors, molecular diameters and activation energies, the rates of formation and hence the quantities produced should be in this same ratio. Assuming the same activation energies, the steric factors (or molecular diameters) must increase in the reverse order. This might imply that the more complex the quasi-molecule the greater the chance of a suitable *three-body collision*, a not unexpected result.

Reactions (8) and (9) involve small heats of reaction and for (8) Rice and Herzfeld give a heat of activation of 10,000 cal. This accounts for the fact that little diketone is formed at the higher temperature.

Summary

1. Photochemical decomposition of ethyl methyl ketone in the near ultraviolet (largely with the 3130 Å. line of mercury) leads to the production of diketones, approximately 11% of the reaction going in this way at room temperature.

2. The quantum yield of carbon monoxide formation from ethyl methyl ketone at room temperature with wave lengths from 1850 to 2000 Å. increases from about 0.70 to about 0.88 as the pressure decreases from 90 mm. to 0.1 mm.

3. Diketones are formed in this region of the spectrum. The formation of biacetyl has been shown spectroscopically.

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[14] Rice and Herzfeld, THIS JOURNAL, 56, 284 (1934).

4. The total quantum yield of ethyl methyl ketone decomposition with wave lengths below 2000 Å. is nearly one at low pressures when allowance is made for diketone formation.

5. At higher temperatures some methane is formed, but at room temperature the principal hydrocarbons are ethane, propane and butane in approximately equal amounts.

6. Possible secondary reactions have been discussed.

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE INSTITUTE OF TECHNOLOGY OF THE UNIVERSITY OF MINNESOTA]

Studies on Aging and Properties of Precipitates. XXIII. The Postprecipitation of Ferrous Sulfide with Cupric Sulfide

BY I. M. KOLTHOFF AND FRANK S. GRIFFITH[1]

Böttger and Druschke[2] found that iron is found in a precipitate of copper sulfide when the latter is formed under such conditions that no precipitation of iron sulfide alone occurs. Even when the copper sulfide was precipitated from solutions which were 2 N in nitric, hydrochloric or sulfuric acid, iron was found in the precipitate. In the present paper it is shown that iron sulfide is not *co*-precipitated but *post*-precipitated with cupric sulfide.

Experimental

The materials used were C. P. products. The stock ferrous sulfate solution was kept in 0.1 N sulfuric acid, the latter inhibiting the air oxidation. A fresh solution was prepared frequently. Concerning the method of treatment of the solutions with hydrogen sulfide reference is made to previous papers.[3]

After shaking in an atmosphere of hydrogen sulfide for a given period of time the solutions were filtered and the precipitate washed with 0.1 N hydrochloric acid which had been saturated with hydrogen sulfide. The filtrate and washings were evaporated to a volume of 25–50 ml., thus removing the hydrogen sulfide, 5 ml. of 5 N hydrochloric acid was added and any ferric iron formed reduced with a slight excess of stannous chloride. After the further classical treatment the ferrous iron was titrated with 0.05 N potassium dichromate using sodium diphenylamine sulfonate as indicator. In those cases in which the amount of iron removed from solution was very small the iron was determined in the washed precipitate. The latter was dissolved, the iron oxidized and precipitated with ammonia. The precipitate was dissolved, the iron reduced to the ferrous state and titrated with 0.005 N potassium dichromate.

Experimental Results

In order to get an impression of the order of magnitude of the precipitation of iron, various preliminary experiments were carried out. One hundred ml. of solution containing 5 mmol. of cupric sulfate and 1.25 mmol. of ferrous sulfate and being 1.55 N in sulfuric acid (after precipitation of copper 1.65 N) was treated with hydrogen sulfide for fifteen minutes, filtered, and the iron determined in the precipitate. Only 0.05 mg. of iron or 0.07% of the original amount was found in the precipitate. The experiment was repeated with the solution heated to 95° before saturating with hydrogen sulfide; 0.19 mg. of iron (0.27%) was found in the precipitate. A similar set of experiments was run with the solution being 0.53 N in sulfuric acid (after precipitation of copper sulfide 0.63 N): precipitation at room temperature, 0.42 mg. of iron in precipitate (0.60%); precipitation started at 95°, 0.75 mg. of iron in precipitate (1.07%). The amounts of iron found in the precipitates (room temperature) are about one-fifth of those expected from the results of Böttger and Druschke. However, these authors do not state the time of precipitation; it is shown later that the amount of iron entering the precipitate increases with the length of time of contact with the copper sulfide.

Evidence of Postprecipitation: Effect of Time before Filtration, Concentration of Acid and of Temperature.—In the following experiments a mixture was used containing 5 mmol. of copper sulfate and 1.25 mmol. of ferrous sulfate in 100 ml. In some of the experiments the iron was present during the precipitation of the copper sulfide, in others it was added one or two minutes after precipitation of the copper. Hydrogen sulfide was bubbled through continuously during the course of the experiments; in the one-month experiments the gas outlet, after a few hours, had a fine capillary. The flasks were shaken continuously except in the one-month experiments. After the period of shaking given in Table I the filtrates were analyzed for iron.

From the fact that the extent of precipitation of the iron is about the same, regardless of whether the copper sulfide is precipitated in the presence of iron or the iron is added after precipitation of copper, it follows conclusively that we are dealing with a phenomenon of postprecipitation. The amount of postprecipitation decreases rapidly with

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[1] From a thesis submitted by Frank S. Griffith to the Graduate School of the University of Minnesota in partial fulfilment of the requirements for the degree of Doctor of Philosophy, June, 1937.

[2] W. Böttger and K. Druschke, *Ann.*, **453**, 315 (1927).

[3] I. M. Kolthoff and D. R. Moltzau, *J. Phys. Chem.*, **40**, 779 (1936); Kolthoff and Griffith, *ibid.*, **42**, 531 (1938); see also thesis of junior author.[1]