has a composition corresponding to a 1:1 copolymer of oxygen and styrene. This copolymer contains of the order of 40 styrene peroxide units.

A chain mechanism has been proposed to account for the observed kinetics and products of the reaction of styrene with oxygen during the oxygen induction period. The rate of copolymerization of styrene with oxygen is of the order of a thousandth smaller than the normal rate of emulsion polymerization of styrene in a recipe containing the standard amount of soap.

MINNEAPOLIS, MINN. RECEIVED FEBRUARY 21, 1947

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

Photochemical Studies. XXXVIII. A Further Study of the Photochemistry of Methyl *n*-Butyl Ketone

BY WALLACE DAVIS, JR.,[1] AND W. ALBERT NOYES, JR.

The photochemical decomposition of methyl *n*-butyl ketone was first studied by Norrish and his co-workers,[2] who showed that there are two reactions, one to give acetone and propylene, the other to give carbon monoxide and a series of other compounds, mostly hydrocarbons. Bamford and Norrish concluded that the reaction giving acetone and propylene proceeds without intermediate free radicals whereas the second does involve free radicals. It has been shown, however, that the acetone–propylene reaction might be explained by a series of free radical reactions.[3] The ratio of acetone to propylene was about 3:4,[4] but was not very precisely determined.

The evidence for or against free radicals in the production of acetone and propylene in the gas phase reaction was based mainly on the invariance of quantum yield with varying conditions. The reaction in paraffin solution performed by Bamford and Norrish also indicated that no unsaturation accompanied this reaction other than that due to the propylene itself, and this further supported the idea that free radicals are not involved. The evidence, while reasonably good, was not conclusive, and the work described in the present paper was designed to answer several important questions.

Experimental

A General Electric Company Type AH-6 high-pressure mercury arc, red purple corex glass, and filter solutions of nickel chloride, potassium acid phthalate, and potassium chromate[5] were used to give approximately monochromatic radiation of wave lengths 3130 Å. This arc operates at such a high pressure that the emission lines are exceedingly broad. A slight change in operating conditions may produce an appreciable change in the wave length–intensity distribution of this arc-filter combination. Since the absorption coefficient of methyl *n*-butyl ketone (and, in general, of all other ketones) is changing quite rapidly with wave length near 3130 Å., it is evident that measurements with this type of light source do not correspond to monochromatic light and might not be very reproducible. However, surprisingly good constancy was found for the "integrated" absorption coefficient in these experiments. The absorption should be obtained in each individual experiment.

The absolute values of the quantum yield are referred to acetone vapor at 120° as a primary standard. The quantum yield of carbon monoxide formation from acetone at that temperature is unity.[6] Since the acetone and methyl *n*-butyl ketone were used in the same cell with the same light source, all corrections for window reflection would be negligible providing the percentage absorptions in the two cases were identical. In general, however, the acetone pressure was higher and corrections for window reflection were necessary, although small.

The corrections for transmission and absorption by windows were applied as follows:[7]

Let α be the fraction of light absorbed by a single window with a single passage of light, and let it be assumed that the two windows of the cell are identical. Let F = fraction of light reflected at a gas–quartz interface and β = the fraction of light absorbed by the gas during a single passage of light. After multiple reflections it can be shown that the fraction of the incident light reflected by one window is

$$R = F\left[1 + \frac{(1-F)^2(1-\alpha)^2}{1-(1-\alpha)^2F^2}\right] \qquad (1)$$

The fraction of incident light absorbed by one window is

$$A = \frac{(1-F)\alpha}{1-(1-\alpha)F} \qquad (2)$$

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[1] National Research Council Predoctoral Fellow, 1945–1946. Part of the work described in this article was performed under Contract N6onr-241, Task I with the United States Navy.

[2] R. G. W. Norrish and M. E. S. Appleyard, *J. Chem. Soc.*, 874 (1934); C. H. Bamford and R. G. W. Norrish, *ibid.*, 1538 (1938); B. M. Bloch and R. G. W. Norrish, *ibid.*, 1638 (1935).

[3] J. E. Wilson and W. A. Noyes, Jr., THIS JOURNAL, **65**, 1547 (1943).

[4] See also W. Davis, Jr., and W. A. Noyes, Jr., *ibid.*, **64**, 2376 (1942).

[5] R. E. Hunt and W. Davis, Jr., *ibid.*, **69**, 1415 (1947).

[6] D. S. Herr and W. A. Noyes, Jr., *ibid.*, **62**, 2052 (1940).

[7] For details of the derivations of the equations in the following paragraphs see R. E. Hunt and T. L. Hill, *J. Chem. Phys.*, **15**, 111 (1947).

and the fraction transmitted by one window becomes

$$T = \frac{(1 - F)^2(1 - \alpha)}{1 - (1 - \alpha)^2F^2} \qquad (3)$$

If I_0 is the intensity of light at normal incidence on a cell having two identical parallel windows and I_T is the light transmitted through the second window, one can now show that

$$I_T = \frac{I_0T^2(1 - \beta)}{1 - (1 - \beta)^2R^2} \qquad (4)$$

F is given by the expression

$$F = \left(\frac{n - 1}{n + 1}\right)^2 = 0.0381 \qquad (5)$$

based on an index of refraction of 1.485 for quartz at 3130 Å. $I_T/I_0 = 0.692$ if $\beta = 0$ and $\alpha = 0.104$ (the value of α for the cell used in this work). Hence $R = 0.06643$.

Experimentally, I_T is determined for $\beta = 0$ and for $\beta > 0$; *i. e.*, I_{T_0} and I_{T_β} are the experimentally measured quantities. These quantities are related to each other by the expression

$$\frac{I_{T_0} - I_{T_\beta}}{I_{T_0}} = \frac{[1 + (1 - \beta)R^2]\beta}{1 - (1 - \beta)^2R^2} \qquad (6)$$

Thus it is possible to determine β and hence I_a, the loss in intensity due to absorption by the gas. I_0 is of no direct importance but rather that part of I_0 which passes through the cell interior, namely, I_i.

$$I_a/I_{i_\beta} = \beta \qquad (7)$$

where I_{i_β} is given by

$$\frac{I_{i_\beta}}{I_{T_0}} = \frac{(1 - R^2)}{T[1 - (1 - \beta)R]} \qquad (8)$$

It can be shown that $(I_{T_0} - I_{T_\beta})/I_{T_0}$ is very close to β, the difference being in all cases less than 1% even for very low percentage absorption. From a knowledge of I_{T_0} and I_{T_β} one can calculate the true percentage of absorption and hence the absolute energy loss.

For methyl *n*-butyl ketone $(I_{T_0} - I_{T_\beta})I_{T_0}$ is only about 0.08 at 100° and 33 mm. pressure. Hence, the difference $I_{T_0} - I_{T_\beta}$ is subject to considerable error. For this reason the function $(I_{T_0} - I_{T_\beta})/I_{T_0}$ (taken as equal to β) was determined fourteen times at 100° at varying pressures and a straight line plot through the origin was made. Since $(I_{T_0} - I_{T_\beta})/I_{T_0}$ had been determined as a function of pressure, it was unnecessary during the course of a run to determine I_{T_0}. From

$$\frac{I_a}{I_{i_\beta}} \times \frac{I_{i_\beta}}{I_{T_\beta}} = \frac{I_a}{I_{T_\beta}} \qquad (9)$$

it is possible from a plot of I_a/I_{T_β} *vs.* β to calculate I_a from β and I_{T_β}.

By use of acetone at 120° the intensity in quanta per second corresponding to unit deflection with a photocell galvanometer circuit can be used to obtain the intensity in quanta per second from corresponding data for methyl *n*-butyl ketone. It is assumed that one molecule of carbon monoxide is formed per quantum absorbed in acetone at a temperature of 120°.

No correction has yet been made due to reflection from the window of the photocell. This correction would be zero if the transmitted intensity were the same in the calibration as in the actual experiment. The maximum error amounts to about 4% and is not dependent very markedly on the value of β. In this work the photocell reflection errors largely cancelled, the final error due to this being only about 1%. Consequently this correction is neglected.

Table I shows the data necessary for calculating the value of I_a from β and I_{T_β}.

TABLE I

DATA FOR CALCULATION OF ABSORBED LIGHT FROM TRANSMITTED LIGHT

$I_a/I_{i_\beta} = \beta$	$\frac{I_{T_0} - I_{T_\beta}}{I_{T_0}} = \frac{[R^2(1 - \beta) + 1]\beta}{1 - (1 - \beta)^2R^2}$	$\frac{\frac{I_{T_0} - I_{T_\beta}}{I_{T_0}} - \frac{I}{I_{i_\beta}}}{I_a/I_{i_\beta}} \times 100$	I_{i_β}/I_{T_β}	I_a/I_{T_β}
0.01	0.010087	0.87	1.2951	0.01295
.02	.020172	.86	1.3074	.02615
.03	.030253	.84	1.3200	.03960
.04	.040333	.83	1.3328	.05331
.05	.050409	.81	1.3459	.06730
.06	.060484	.81	1.3592	.08155
.07	.070555	.79	1.3728	.09610
.08	.080625	.78	1.3868	.11094
.09	.090692	.77	1.4010	.12609
.10	.10076	.76	1.4157	.14157
.11	.11082	.75	1.4305	.15736
.12	.12088	.73	1.4458	.17350
.13	.13094	.72	1.4613	.18997
.14	.14100	.71	1.4773	.20682
.15	.15104	.69	1.4936	.22404
.20	.20129	.65	1.5814	.31628
.25	.25144	.58	1.6810	.42025
.30	.30158	.53	1.7947	.53941
.35	.35166	.47	1.9261	.67414
.40	.40171	.43	2.0794	.83176
.45	.45169	.38	2.2606	1.01727
.50	.50166	.33	2.4781	1.23905
.55	.55157	.29	2.7440	1.50920
.60	.60148	.25	3.0764	1.84584
.65	.65136	.21	3.5039	2.27754
.70	.70120	.17	4.0741	2.85187

Methyl *n*-butyl ketone (Eastman Kodak Co. C.P.) was purified by recrystallization of the semicarbazone from hot 25% ethyl alcohol. After decomposition of the semicarbazone the ketone was separated by a separatory funnel and treated with anhydrous cupric sulfate to remove water. Finally the ketone was distilled from anhydrous cupric sulfate and C.P. sodium hydroxide pellets, the middle third being retained for use.

The acetone for use in the actinometer was

Eastman Kodak Co. C.P., dried and distilled in the same manner as the methyl *n*-butyl ketone, the middle fifth being taken.

The apparatus was constructed of Pyrex except for the quartz reaction cell. Between 3×10^{-8} and 5×10^{-6} mole of gas could be analyzed, the method being somewhat similar to that used in previous research in this Laboratory.[8] The U-tube containing copper oxide heated to 200° oxidizes only carbon monoxide from the liquid nitrogen fraction. Three tubes containing platinum filaments allowed for the simultaneous combustion of three products (or of one in triplicate). The platinum wire was heated to about 600° and about twice the stoichiometric amount of oxygen was used. Dry Ice traps removed most of the mercury from the tubes containing the filaments.

The combustion analyses gave 5 to 10% accuracy in the carbon : hydrogen : oxygen ratio, but further information on the nature of the products was essential. A modified Ward apparatus[9] (see Fig. 1) was used not only to control the fractionation temperature (measured on a six-junction copper–constantan thermopile) but also to obtain vapor pressure data. These two operations were performed on all products not condensed by Dry Ice. The products uncondensed by liquid nitrogen (CO, CH_4 and C_2H_6) were removed and analyzed. Then the temperature in the Ward apparatus was allowed to rise slowly to about −160°. The C_3 hydrocarbons appear at about −175° and could be removed and analyzed. At about −150° a major fraction showing between four and five carbon atoms per molecule appeared. The vapor pressures of these materials in the range of −150 to −130° indicated that they were probably hydrocarbons. The fourth fraction which analyzed as C_3H_4 (or C_3H_6O) was probably acetone. Its vapor pressure at −95° was found to be about 20 microns.

Figure 2 shows that there are four major fractionation temperatures: (1) CO, C_2H_6, CH_4 at −188 to −195°; (2) C_3 (C_3H_6, C_3H_8) at about −165°; (3) C_4 and C_5 hydrocarbons (not unequivocally identified) at −135 to −150°; (4) acetone at −95°. Comparison of the vapor pressures with the data of Lucas[10] and of Zook, Oakwood and Whitmore[11] permitted an estimation to be made of the nature of the products.

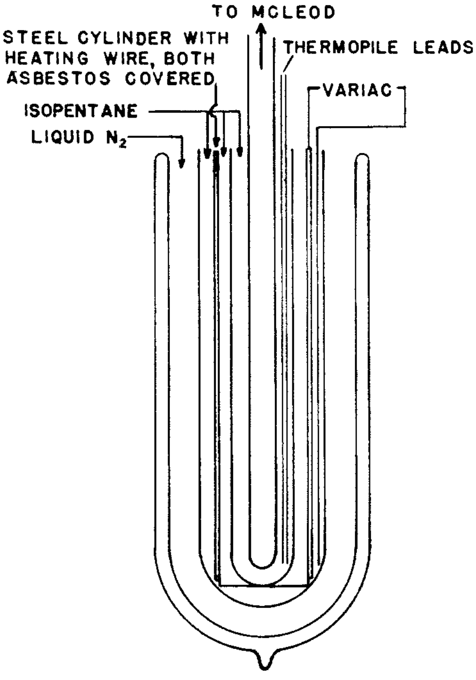

Fig. 1.—Modified Ward apparatus.

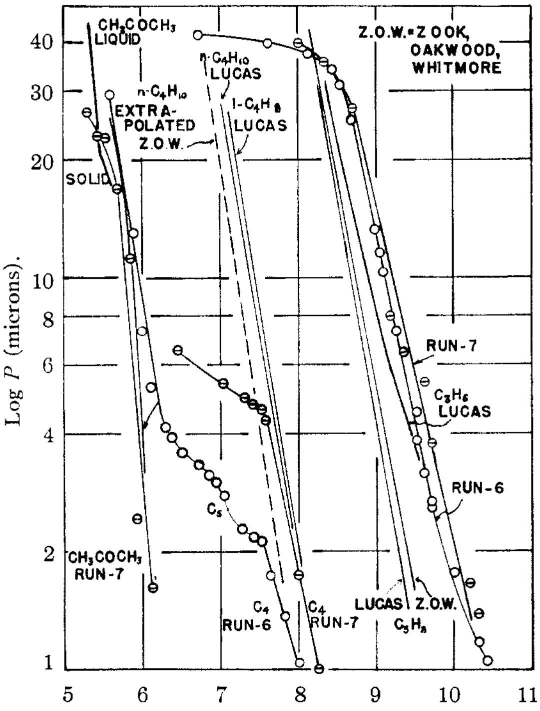

Fig. 2.

Experimental Results

Some qualitative runs were made first without measuring light intensity merely to determine the effect of temperature upon the nature of the products. Table II shows the results of these runs.

In these runs the incident intensity was kept as constant as possible. At constant pressure the number of absorbing molecules per cubic centimeter decreases with increasing temperature. However, the form of the absorption coefficient–temperature curve changes with temperature so that the absorbed intensity changed less than experimental error with increase in temperature.

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

(9) E. C. Ward, *Ind. Eng. Chem., Anal. Ed.*, **10**, 169 (1938).

(10) R. Lucas, *Compt. rend.*, **204**, 493 (1937).

(11) Zook, Oakwood and Whitmore, private communication to Dr. W. D. Walters.

TABLE II

EFFECT OF TEMPERATURE, $(CH_3)_2CO$, AND N_2 ON THE RATE OF FORMATION OF THE PRODUCTS OF THE λ2900–3200 DECOMPOSITION OF METHYL *n*-BUTYL KETONE

$P_{ketone} = 12 \pm 1$ mm., I_0 = constant

Run	Temp., °C.	Rate of formation of products: molecules × 10^{-17} per hour CO	CH_4	C_2H_6	CO + CH_4 + C_2H_6	C_3H_6	C_4	C_5	$(CH_3)_2CO$
1	25	...	...	...	0.03	0.99	0.3		0.95
2	25	...	...	...	.05	.92	> .1		..
3	25	...	...	...	.05	1.0	.14	.09	.81
4	27	0.035	...	0.008	.043	0.91	.10	.01	.78
5	105	.153	0.062	.080	.295	.99	.16	.06	.54
6[a,c]	105	.167	.061	.026	.254	1.123	0.085		.90
7[a,c]	215	.329	.228	.049	.606	1.218	0.164–0.178		.75
8[a,c]	300	⩽ .7	.111	.667	1.853	1.98	.48		.96
			− .491	−1.047					
10[c]	100	...	...	...	...	1.045	.64[b]		..
13 mm. $(CH_3)_2CO$ present									
11[c]	100	...	...	...	...	1.35	.18		.79
150 mm. N_2 present									

[a] Flow runs. [b] Assuming $C_4 = C_5$. [c] Fractionation using Ward apparatus.

Acetone yields are all probably too low in these runs. It was not until quantitative runs were made (Table III) that the full difficulty of separating acetone from the methyl *n*-butyl ketone was appreciated. At least ten successive distillations of half to one hour from −78 to −195° followed by removal of the acetone by a Toepler pump were necessary to approach complete removal of the acetone.

TABLE III

QUANTUM YIELDS AT 103° AND 3130 Å.

Run	P_{ketone}, mm.	I_a/sec.	Φ_{CO}	$\Phi_{CO+CH_4+C_2H_6}$	$\Phi_{C_3H_6}$	$\Phi_{C_4+C_5}$	$\Phi_{(CH_3)_2CO}$
12	13	4.39×10^{13}	..	0.095	0.389	0.01	(0.187)
13	34.5	6.23	..	.139	.520	.195	.515
14	33	6.60	0.11	.172	.487	.181	.484
15	33	0.803	..	.252	.426	.252	.585
16	33	0.788	.05	.086	.414	.073	.441
					Av. .45		Av. .51

In run 12 the full difficulty of recovering the acetone was not appreciated, and the yield for this substance is certainly low. This value is not included in the average. The yields of propylene are probably more accurate than any of the others given.

Table III gives the data on the quantum yields of the products. The data are not as accurate as might be desired, but it is evident that the more care taken to collect the acetone completely, the more nearly the ratio of acetone to propylene approaches unity. The difficulty of removing all of the acetone was not fully appreciated in Run 12.

Discussion of Results

It is evident from the results given in the preceding section that at room temperature and at temperatures up to about 100° the ratio of acetone to propylene is approximately 1:1. The qualitative runs indicate, moreover, that the acetone yield is virtually independent of temperature up to nearly 300°.

The results of Norrish and his co-workers[2] are essentially confirmed in the sense that there are two reactions, but these results show further that one of these reactions (acetone and propylene formation) is virtually temperature independent whereas the other (carbon monoxide plus other products) varies markedly with temperature.

Evidence from many different sources[12] indicates that the radical CH_3CO is very unstable at temperatures of 100° and above. The energy of activation for the reaction

$$CH_3CO = CH_3 + CO \qquad (10)$$

may be as low as 10 kcal. The formation of acetone at 300° in the present experiments cannot be ascribed, therefore, to any reaction which involves the CH_3CO radical as an intermediate. Moreover, the invariance of the acetone yield with temperature, with intensity, and with pressure tends to indicate that it is formed in a single step after the absorption of light. This is in agreement with the conclusions of Bamford and Norrish in paraffin solution.[2]

The second type of reaction which leads to carbon monoxide and various other products has a rate dependent quite markedly on temperature. The effects of other variables have not been adequately determined. The earlier work,[3] however, did indicate that there was no appreciable variation with intensity. This is a matter which demands further investigation.

[12] M. Barak and D. W. G. Style, *Nature*, **135**, 307 (1935); R. Spence and W. Wild, *ibid.*, **138**, 206 (1936); for a summary see W. A. Noyes, Jr., and P. A. Leighton, "Photochemistry of Gases," Reinhold Publishing Company, New York, N. Y., 1941, p. 358; E. W. R. Steacie, "Atomic and Free Radical Reactions," Reinhold Publishing Corp., New York, N. Y., 1946, p. 379.

Tentatively we may write

$$CH_3COC_4H_9 + h\nu = CH_3COCH_3 + C_3H_6;\ \Phi_1 = 0.4\text{–}0.5 \qquad (11)$$

The fate of the remaining molecules which absorb light is of some interest. There is no positive indication that chain reactions occur even at temperatures of 300°. Since the yield of carbon monoxide has not been determined definitely at that temperature, it may be estimated only from the relative rates contained in Table II. On this basis the rate at 300° may be as much as 10 to 12 times the rate observed at 25°. This would indicate a yield of the order of magnitude of 0.5 to 0.6. In other words, the total yield of carbon monoxide plus acetone at 300° is of the order of magnitude of unity although there is no indication that the carbon monoxide yield has ceased to rise at that temperature.

The rise in yield of carbon monoxide and of other products with temperature might be due to one of three causes: (1) the instability of certain radicals which might otherwise recombine to form methyl *n*-butyl ketone; (2) an increased yield in the primary decomposition with rise in temperature.

No fluorescence of methyl *n*-butyl ketone has been reported, but such fluorescence would be extremely weak and very difficult to study. There is no adequate basis, however, for assuming that we are dealing here with activated molecules which can fluoresce. The low over-all yield of methyl *n*-butyl ketone disappearance is probably to be ascribed to a low yield in the primary process. The act of absorption in a complex molecule of this type may lead to changes in the force constants of several bonds and the Franck–Condon principle may necessitate the activation of a complex set of vibrations. If the molecule, as a result of possessing higher thermal energy, is already executing a complicated vibration in the ground state prior to absorption, the nature of the vibrations in the upper state may well be different from those which would be produced by "colder" molecules. In general, therefore, the primary quantum yield may be a function of temperature although it is not implied that a bond necessarily breaks instantaneously, that is, in a period shorter than one vibration.

The possibility that the decomposition into carbon monoxide and hydrocarbons results from a chain type reaction must not be ignored, although lack of dependence of yields on various variables does not lend support to this idea. If part of the molecules activated by the primary process may be deactivated by collisions and the others dissociate one obtains the following set of equations

$$CH_3COC_4H_9 + h\nu = CH_3COC_4H_9^* + d(K^*)/dt = k_1I_a \qquad (12)$$

$$CH_3COC_4H_9^* = CO + \text{other products};\ -d(K^*)/dt = k_2(K^*) \qquad (13)$$

$$CH_3COC_4H_9^* + M = CH_3COC_4H_9 + M;\ -d(K^*)/dt = k_3(K^*)(M) \qquad (14)$$

where (K*) represents the concentration of activated molecules and (M) is the concentration of possible deactivating molecules, in this case the concentration of methyl *n*-butyl ketone since no foreign gas was present. By making the customary assumptions regarding the steady state, one finds that

$$+\frac{d(CO)}{dt} = \Phi_{CO}I_a = \frac{k_1I_a}{1 + k_3(M)/k_2} \qquad (15)$$

It should be noted that equation (15) would also be valid if the reaction were of the chain type unless the chain length were dependent on total pressure.

From the values of the carbon monoxide yield at various temperatures and putting $k_1 = 0.5$, one can calculate $k_3(M)/k_2$ to be 27.5, 5.25, 2.03 and 0.42 at 300, 378, 488 and 573° K., respectively. Thus the quantum yield of carbon monoxide formation should be a decided function of total pressure, particularly at low temperatures. Data on this point are not extensive but indicate much less variation than would be predicted from equation (15). Collisional deactivation appears not to be very important. If a chain mechanism is adopted the length of chain would have to be independent of total pressure.

At the higher parts of the temperature range investigated the reaction may well be of the chain type, but too little is known at present to make plausible suggestions concerning the mechanism. Data soon to be published on other ketones may throw some light on this point.

An alternative to equation (14) may be suggested

$$CH_3COC_4H_9^* = CH_3COC_4H_9^{**};\ -d(K^*)/dt = k_4(K^*) \qquad (16)$$

where $CH_3COC_4H_9^{**}$ may be taken to represent a molecule with the energy so distributed among the degrees of freedom that decomposition is exceedingly improbable. Equation (15) is now replaced by

$$+\frac{d(CO)}{dt} = \Phi_{CO}I_a = \frac{k_1I_a}{1 + k_4/k_2} \qquad (17)$$

where k_4/k_2 will have the same numerical values as found for $R_3(M)R_2$ above.

From the variation of k_4/k_2 with temperature an empirical energy of activation of about 4500 calories is obtained. The exact meaning of this quantity cannot be stated. This may mean that when the absorbing molecules possess more thermal energy, the probability of dissociation into radicals which eventually yield carbon monoxide relative to mere degradation into vibrational energy increases. This activation energy might apply also to some step in a chain mechanism, although it is not believed that chains are initiated in the lower part of the temperature interval studied.

It is interesting to note that Bamford and Norrish[13] for di-*n*-propyl ketone found the yield

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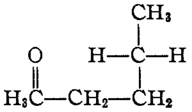
[13] C. H. Bamford and R. G. W. Norrish, *J. Chem. Soc.*, 1544 (1938).

of carbon monoxide to increase from 0.26 at 15° to 0.37 at 100° in the vapor phase whereas the yield in paraffin solution increased from 0.01 to 0.30 in the same temperature interval. The difference between the two cases may be due to the Franck–Rabinowitch effect. The yield of ethylene decreased in both cases with increase in temperature, but the change was not very pronounced. Thus the general phenomena in di-*n*-propyl ketone and in methyl *n*-butyl ketone are similar.

The formation of acetone and propylene in what appears to be a single step with yield independent of temperature is an interesting phenomenon. Possibly methyl *n*-butyl ketone can exist in a cyclic form through hydrogen bonding



which might be expected to dissociate into the enol form of acetone and propylene in a single step. The quantum yield of 0.5 might indicate 50% of the molecules to be in this form but, if this is correct, the independence of temperature is surprising.

By placing deuterium atoms on the γ-carbon only it might be possible to obtain evidence for the cyclic mechanism if the acetone can be shown to possess one deuterium atom per molecule. Deuterium atoms in other positions would not lead to deuterated acetone if the picture is valid.

It should be possible to put C^{14} in the two α-positions and in the carbonyl group. In this case every molecule of acetone should have three radioactive carbon atoms.

Experiments of these two types are to be undertaken as soon as circumstances permit.

Summary

1. Methyl *n*-butyl ketone gives a quantum yield of acetone production of about 0.5 independent of temperature from 25 to 300°.
2. The quantum yield of carbon monoxide formation increases markedly with temperature.
3. One molecule of propylene is produced for each molecule of acetone at room temperature, but the yields of propylene and of several other hydrocarbons increase markedly with temperature.
4. Acetone is not formed from a recombination reaction or any other reaction involving acetyl radicals since the latter are too unstable at the higher temperatures employed.
5. It is probable that acetone and propylene with quantum yields of about 0.5 are formed in the primary step whereas the remainder of the absorbing molecules either give radicals which eventually produce carbon monoxide or have the energy degraded into vibrational energy. Increase in the thermal energy of the absorbing molecules increases the probability of this type of decomposition.

ROCHESTER, NEW YORK RECEIVED APRIL 25, 1947

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE PITTSBURGH PLATE GLASS CO., COLUMBIA CHEMICAL DIVISION]

A Study of the Reaction of Alcohols with Thionyl Chloride[1]

BY WILLIAM E. BISSINGER AND FREDERICK E. KUNG

As illustrated in the following equations, thionyl chloride has been reported[2–7] to undergo a wide variety of reactions with alcohols in the absence of hydrogen chloride acceptors.

$$SOCl_2 + ROH \longrightarrow ROSOCl + HCl \quad (1)$$
$$ROSOCl + ROH \longrightarrow R_2SO_3 + HCl \quad (2)$$
$$SOCl_2 + 2ROH \longrightarrow R_2SO_3 + 2HCl \quad (3)$$
$$R_2SO_3 + SOCl_2 \longrightarrow 2ROSOCl \quad (4)$$
$$ROSOCl \longrightarrow RCl + SO_2 \quad (5)$$
$$SOCl_2 + ROH \longrightarrow \text{olefin} + 2HCl + SO_2 \quad (6)$$

In some of these reactions considerable disagreement exists with regard to the reaction products and the yields obtained.[7,8,9] The most serious discrepancies are found in the results obtained from the reaction of secondary alcohols with thionyl chloride. For example, although Voss and Blancke[10] have reported the preparation of isopropyl chlorosulfinate in 46% yield, Gerrard[8] has claimed a 75–80% yield, while Libermann[7] stated that "only very small quantities" of impure isopropyl, *s*-butyl, and *s*-octyl chlorosulfinates could be obtained from the direct reaction of these alcohols with thionyl chloride. Another controversy over the preparation of cyclohexyl sulfite from cyclohexyl alcohol and thionyl chloride was recently disposed of by Kyrides.[9] Some factors which may be responsible for these anomalies are (a) the frequent failure of various workers to present experimental details, (b) the sensitivity of some of these reactions to small changes in experimental conditions due to (c) the known thermal instability of the alkyl chlorosulfinates and (d) the previously unreported rapid rate of reaction of sulfite esters with hydrogen chloride. In

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(1) Presented before the Division of Organic Chemistry at the Atlantic City Meeting of the American Chemical Society, April 17, 1947.

(2) Carius, *Ann.*, **111**, 95 (1859).

(3) Stahler and Schirm, *Ber.*, **44**, 319 (1911).

(4) Geuther and Roschlau, *Ann.*, **224**, 223 (1884).

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