noted here: methyl compounds of the less electronegative P and Sb are spontaneously inflammable but those of the more electronegative As and Bi are not.

Oxidation by carbon dioxide occurs readily for the compounds with most negative methyl but is slight or negligible where the charge on methyl is less than −0.15.

Hydrolysis.—As might be expected, hydrolysis of methyl compounds capable of both reaction with carbon doxide and spontaneous inflammation in air is violent. As the charge on methyl becomes less than −0.07, only the methyl compounds of Ga, In and Tl are appreciably susceptible to attack by water, and these, stepwise, the intermediates being stable. It is evidently necessary to provide an unoccupied orbital. The unreactivity of the boron compound seems somewhat anomalous and may be associated with steric effects.

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The Long Wave Photochemistry of Biacetyl and its Correlation with Fluorescence at Temperatures over 100°

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A study of the photochemistry of biacetyl at 4358 and at 3650 Å. has recently been published.[2] Primary quantum yields were calculated by an equation based on the mechanism of Bell and Blacet.[3] This equation seems satisfactory at temperatures below 100°. At temperatures over 100° the primary quantum yield should be equal to the ethane yield if acetyl radicals and $CH_2COCOCH_3$ radicals dissociate completely.[3] However, the primary yield calculated by equation 14 of the previous paper and the ethane yield do not agree. They should agree if the mechanism is correct and complete. This indicates that steps other than those in the mechanism occur, in agreement with recent findings of Guenther, Whiteman and Walters[4] on the thermal reaction.

It is certain that the primary yield is greater than the ethane yield and it may be below the value calculated by equation 14 of the previous article. Formation of $CH_3COCOCH_2CH_3$ would not vitiate the calculations by equation 14. On the other hand, $(CH_3)_2COHCOCH_3$ or $(CH_3)_2C(OCH_3)COCH_3$ formed from the possible intermediate radical $(CH_3)_2COCOCH_3$[5] would mean that the primary yield is less than that calculated by equation 14. Formation of any of these compounds including $CH_3COCOCH_2CH_3$ would make the primary yield greater than the ethane yield.

Equation 14 should give approximately correct values of the primary yield, although discrepancies may increase with increase in temperature. This equation is used and certain tentative conclusions about the relationship of fluorescence to primary photochemical process are drawn.

Experimental

The apparatus and analytical procedure were the same as those described previously.[2]

Monochromatic light at 4358 Å. was obtained by a combination of Corning Glasses 3389 (2.5 mm.) and 5113 (2.0 mm.). Radiation at 3650 Å. was obtained by Corning Glass 5860 (5.0 mm.). Less than 1% of radiation at 3340 Å. was present. General Electric Company AH.6 mercury arcs were used. The beam completely filled the reaction vessel. Intensity was varied by chrome-alumel neutral density filters.[6]

Results

The results are given in Table I. The primary quantum yields in the sixth column are calculated from equation 14 of the previous article.

The revised activation energy for methane formation given by Ausloos and Steacie[7] has been used to calculate the acetone yield. This calculation would be in error if other compounds than the ones given in the mechanism of Bell and Blacet[3] are formed.

TABLE I

QUANTUM YIELDS FROM BIACETYL AT 4358 AND 3650 Å. AT TEMPERATURES OVER 125°

Cell, 2.3 cm. × 20.0 cm.; temperatures are controlled to about ±1°.

(B) Biacetyl concn. molecules × 10^{-17}/ml.	I_a, quanta × 10^{-12} absorbed/ml./sec.	Φ_{CO}	$\Phi_{C_2H_6}$	Φ_{CH_4}	ϕ	$\frac{R_{CH_4}}{R_{C_2H_6}^{1/2}(B)}$ × 10^{12} molecules$^{-1/2}$ ml.$^{1/2}$ sec.$^{-1/2}$
		4358 Å., 125°				
9.40	117	0.23	0.057	0.032	0.12	1.6
10.2	119	.20	.052	.029	.10	1.4
		4358 Å., 145°				
9.90	47.3	0.41	0.080	0.092	0.18	2.2
9.86	361	.40	.12	.046	.21	2.5
		4358 Å., 174°				
10.0	45.1	0.84	0.14	0.27	0.30	4.8
		4358 Å., 198°				
10.4	4.74	1.52	0.070	0.73	0.42	5.8
9.77	43.0	1.28	.17	.46	.45	7.3
9.59	104	1.00	.16	.32	.39	8.3
9.55	334	.85	.20	.20	.37	8.3
		3650 Å., 124°				
2.98	13.8	0.64	0.22	0.054	0.35	1.5
5.61	17.6	.53	.15	.074	.26	1.4
8.31	37.9	.50	.14	.069	.25	1.4
11.9	17.5	.48	.094	.12	.19	1.4
		3650 Å., 198°				
2.32	13.5	1.08	0.24	0.28	0.45	9.0
5.29	17.3	1.23	.17	.44	.44	8.4
10.2	14.7	1.57	.13	.70	.45	7.3

(1) Hanovia Chemical and Manufacturing Company Predoctoral Fellow during 1953–1954. This work was supported in part by contract with the Office of Naval Research, United States Navy.

(2) G. F. Sheats and W. A. Noyes, Jr., THIS JOURNAL, **77**, 1421 (1955).

(3) W. E. Bell and F. E. Blacet, *ibid.*, **76**, 5332 (1954).

(4) W. B. Guenther, C. A. Whiteman and W. D. Walters, *ibid.*, **77**, 2191 (1955).

(5) B. de B. Darwent, *Discs. Faraday Soc.*, No. 14, 129 (1953).

(6) See R. Gomer and W. A. Noyes, Jr., THIS JOURNAL, **71**, 3390 (1949).

(7) P. Ausloos and E. W. R. Steacie, *Can. J. Chem.*, **33**, 39 (1955).

Discussion

It is seen that $R_{CH_4}/R^{1/2}_{C_2H_6}$ (B) (where R represents rate in molecules per milliliter per second and (B) is the concentration of biacetyl in molecules per milliliter) is reasonably constant at a given temperature, although possibly there is a slight trend at 198°. This would indicate that methane and ethane are formed by customary reactions.[8]

The following points should be noted: (1) primary yields at 4358 Å. are essentially independent of intensity from 125 to 198°. This is in contrast to the results at room temperature[2]; (2) primary yields at 3650 Å. decrease with increase in pressure at 124°. At 198° the trend is uncertain but small. This correlates with the fluorescence efficiency which increases with increase in pressure.[9]

The detailed mechanism of Bell and Blacet[3] will not be repeated, but for sake of discussion the mechanism used to interpret the fluorescence will be given[10]

4358 Å.:

$$B + h\nu = B^* \quad (1)$$

3650 Å.:

$$B + h\nu = B' \quad (2)$$
$$B' = D \quad (3)$$
$$B' = B \quad (4)$$
$$B' + B = B^* + B \quad (5)$$
$$B^* = D \quad (6)$$
$$= B \quad (7)$$
$$= B + h\nu \quad (8)$$
$$= B^{**} \quad (9)$$
$$B^{**} = B + h\nu \quad (10)$$

At 4358 Å. the following relationships are found.

(a) $\phi/Q = k_6/k_9$ if reaction (9) is assumed not to be reversible. (Q = fluorescence efficiency.) This relationship is valid at 100° since neither ϕ nor Q change appreciably with pressure.[2,10]

(b) A plot of log (ϕ/Q) *vs.* $1/T$ shows an activation energy difference of 16.5 kcal. The ratio of frequency factors is $4 \times 10.^9$

(c) $(1 - \phi - Q)/Q = (k_7 + k_8)/k_9$. A plot of the logarithm of this function *vs.* $1/T$ gives an activation energy difference of 7.1 kcal. (It should be noted that only the green, long lived fluorescence efficiency has heretofore been studied.)[10] Thus if k_8 is small compared to k_7, as it should be since the blue fluorescence efficiency is very low, the activation energy difference between k_7 and k_9 is approximately 7.1 kcal. a_7/a_9, the ratio of pre-exponential factors, is about 3×10^5 by extrapolation.

(d) By subtraction one finds $E_6 - E_7 = 9.4$ kcal. The ratio of pre-exponential factors a_6/a_7 is about 10^4.

By combining the above relationships one finds

$$1/Q - 1 = 4 \times 10^9 \exp(-16500/RT) + 3 \times 10^5 \exp(-7100/RT) \quad (11)$$

since $(1 - \phi - Q)/Q = (1/Q - 1) - \phi/Q$. Equation 11 reproduces satisfactorily the fluorescence data from 75 to 200°.

Thus at 4358 Å. the fluorescence data and the photochemical primary yields as calculated by equation 14 of the previous article can be related to each other. This does not prove, of course, that the detailed mechanism is correct, but it does show that the mechanism fits the facts now known at this wave length.

At 3650 Å. the following relationships are found.

(a) Equation 24 of the previous article states that a plot of $1/\phi$ *vs.* (B) at constant temperature should give a straight line. This assumes that dissociation from (3) predominates over that from (6). This relationship is valid at 124° but at 200° the apparent primary yield does not change with pressure. This may indicate that (6) has become important but since there are doubts about the calculation of the primary quantum yield further speculation is not warranted.

(b) In the previous article Q/ϕ is proportional to (B) at 30°. This assumes dissociation to be due to (3). At 200° the fluorescence efficiency increases with pressure, but the apparent primary yield does not change. Hence this relationship is not valid if the method of calculating the primary yield is correct.

Little more can be said about interpretation either of the fluorescence yields or of the primary photochemical yields at the present time. A method of obtaining the primary yields with precision is badly needed. It is not obvious how these can be obtained since addition of foreign molecules such as iodine, oxygen and nitric oxide will almost certainly change these yields. If all products, including those of minor importance, were known and a completely valid mechanism established, possibly primary yields could be calculated. Such a method would necessitate an accuracy hitherto not attained in quantum yield measurements and a full understanding of diffusion and of wall effects.

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(8) See R. E. Varnerin, This Journal, **77**, 1426 (1955).

(9) H. J. Groh, Jr., *J. Chem. Phys.*, **21**, 674 (1953). This article gives references to an earlier work.

(10) N. A. Coward and W. A. Noyes, Jr., *ibid.*, **22**, 1207 (1954).

Reaction at High Temperatures between Air and Liquid Metal Solutions Containing Sodium. Effect of Solution Composition

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Studies have been made of the reaction between air at room temperature and jets of liquid metal solutions containing sodium at temperatures of 600 to 800°. The reactivity of these solutions showed a marked dependence on solution composition. This behavior is reported here.

The method of study was as follows. A heated alloy was ejected downward through a small orifice into a large steel chamber. The chamber had previously been evacuated and filled with dry air at a pressure of one-fourth to one atmosphere to give a measured dew point of −43°. In all experiments the amount of oxygen in the chamber was from three to thirty times the amount required for complete oxidation of the sodium present. The time-of-flight of a jet through the reaction chamber