correct. This point warrants further study.

Acknowledgments.—The author wishes to thank Mr. T. W. Thoburn for invaluable technical assistance and Dr. R. D. Dunlap for a sample of perfluorohexane.

LEWISTON, MAINE

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

Photochemical Studies. LI. The Photochemistry of Biacetyl at 3650 and 4358 Å. and its Relationship to Fluorescence[1]

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RECEIVED SEPTEMBER 25, 1954

Quantum yields of carbon monoxide, of ethane and of methane from biacetyl vapor have been determined at 3650 and 4358 Å. as functions of intensity, of pressure and of temperature up to 100°. A few results were obtained at about 2700 A. to permit correlation with the work of Blacet and Bell. Methods of estimating primary quantum yields are discussed. At room temperature at 2700 and at 4358 Å. equal numbers of methyl and of acetyl radicals seem to be formed in the primary process. At 3650 Å. this primary process may compete with one in which two acetyls are formed. At 4358 Å. at room temperature the yield is proportional to the intensity and only slightly dependent on pressure. At 3650 Å. the yield decreases as the pressure increases, a fact which can be correlated with a corresponding increase in fluorescence efficiency. As the temperature is raised yields at 4358 Å. decrease and then increase at the same time that they become independent of intensity. Many of the photochemical facts can be correlated with the data on fluorescence to provde a fairly consistent picture for the primary process.

The fluorescence of biacetyl vapor has often been studied.[3] At 3650 Å. the fluorescence efficiency increases with increase in pressure, thus suggesting that collisions "stabilize" excited molecules which might otherwise dissociate.[3d,3g] On the basis of this simple picture the photochemical quantum yield would be expected to decrease as the fluorescence efficiency increases. At 4358 Å. pressure has little effect on the fluorescence efficiency and would be expected to have little effect on the photochemical yields. The present work indicates that the photochemical behavior is complicated at this wave length.

The photochemical decomposition of biacetyl vapor has also been investigated[4] but mainly at wave lengths shorter than 3650 Å. The secondary reactions proposed by Blacet and Bell agree well with published facts and as far as can be ascertained with the present work. Little evidence concerning the nature of the primary process is available, although Khan, Norrish and Porter[5] from a study of the flash photolysis conclude that there may be two modes of primary dissociation, one leading to $2CH_3 + 2CO$ and the other to $2CH_3CO$. The present work is in essential agreement with this conclusion, although a slightly different language for describing what takes place is preferred. In biacetyl as in acetone there is some ambiguity arising from the effect of radical recombination reactions in reducing the over-all yields.[6] Constants derived from the work on acetone may be used in estimating primary quantum yields in biacetyl.

A study of the photochemistry of biacetyl at 3650 and at 4358 Å. is considered to be of interest because of the possibility of correlating the photochemical and fluorescence behaviors.

Experimental

The preparation of the biacetyl has been described.[3l] Analyses for methane, ethane and carbon monoxide were performed by techniques which have been described in earlier papers from this Laboratory. Monochromatic 3650 Å. radiation was obtained in the preliminary runs by a combination of Corning glasses 5840 and 7380. In all runs reported in Table I, 5 mm. of No. 5860 were used alone. Wave length 4358 Å. was obtained by a combination of Corning glasses No. 3389 (2.5 mm.) and 5113 (2.0 mm.). The filter for 2700 Å. has been described.[7] General Electric Co. AH-6 and British Thompson-Houston Type ME/D lamps were used.

Estimates of quantum yields were made by measurement of the fraction of the incident radiation absorbed with an S5 response photoelectric cell. The intensity of the incident radiation at 3130 Å. (later at 2700 Å.) was measured by use of diethyl ketone at 75° for which the quantum yield of carbon monoxide is unity. From the sensitivities of the photocell at various wave lengths the incident intensities at 3650 and at 4358 Å. could be measured with an accuracy of about 20%. At these two wave lengths quantum yields are markedly dependent on conditions so that it would be very difficult to achieve high reproducibility in any case.

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(1) This work was supported in part by contract between the Office of Naval Research, United States Navy, and the University of Rochester. The authors wish to thank Mr. Edwin Becker who did some of the preliminary work as part of a senior research project during 1951–1952.

(2) Hanovia Chemical and Manufacturing Company Predoctoral Fellow during 1953–1954.

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Results

Quantum yields are all low at 3650 and 4358 Å. Even at 100° where there is a short chain reaction[4e,f] the carbon monoxide yield is only about 0.3 to 0.5. The primary quantum yield is thus probably always small under the conditions investigated.

A plot of $R_{CH_4}/R^{1/2}_{C_2H_6}$ *vs.* (B) (where R_{CH_4} and $R_{C_2H_6}$ are rates of formation of methane and of ethane, respectively, in molecules per milliliter per second and (B) is the concentration of biacetyl) should give a straight line[8] provided CH_4 is formed by reaction of methyl radicals with biacetyl and ethane by the second-order combination of methyl radicals. In acetone good straight lines are found and a constant value for the activation energy of methane formation above 100°,[9] but at lower temperatures other effects must be considered.[10] In the present experiments methane is in general too high at room temperature and becomes progressively higher than predicted the higher the intensity. The detailed explanation of this effect must be based on further work but no serious errors would be introduced in the calculations which follow by neglecting this effect.

TABLE I

QUANTUM YIELDS IN BIACETYL

Cell: 2.5 × 20 cm. Radiation assumed to fill cell uniformly in calculating I_a. Primary quantum yields calculated by eq. 14, (a) by assuming $CH_2COCOCH_3$ combines with CH_3; (b) $CH_2COCOCH_3$ decomposes.

Concn. molecules × 10^{-17}/ml. (B)	I_a, quanta × 10^{-12}/ml. sec.	Φ_{CO}	$\Phi_{C_2H_6}$	Φ_{CH_4}	ϕ (a)	ϕ (b)
4358 Å., 100°						
3.00	110	0.048	0.0092	0.0022	0.041	0.042
9.96	109	.066	.013	.0074	.043	.046
15.3	140	.067	.013	.0094	.041	.044
15.0	27.6	.083	.011	.019	.041	.047
15.1	520	.063	.013	.0055	.045	.047
3650 Å., 100°						
3.00	13.4	0.36	0.11	0.021	0.22	0.22
6.05	13.1	.37	.12	.041	.17	.18
10.2	11.5	.32	.08	.059	.14	.15
14.9	11.3	.28	.051	.067	.11	.12
14.8	48.5	.25	.063	.038	.12	.13
15.1	124	.21	.065	.023	.11	.11
2700 Å., 100°						
3.04	14.7	1.11	0.41	0.041	0.64	0.64
10.0	14.7	1.14	.37	.11	.57	.58
15.2	15.6	0.88	.26	.12	.41	.41
4358 Å., 75°						
3.10	52.8	0.00423	0.00029	0.00018	0.0068	0.0071
6.46	54.1	.0066	.00056	.00054	.0077	.010
10.3	49.2	.012	.0012	.0014	.010	.012
15.0	55.0	.014	.0014	.0021	.010	.012
14.8	120	.015	.0021	.0018	.012	.013
15.1	316	.014	.0023	.0012	.012	.013
14.9	482	.016	.0027	.0011	.014	.014
3650 Å., 75°						
3.13	8.90	0.22	0.049	0.0090	0.17	0.18
10.4	7.99	.21	.047	.026	.12	.12
14.8	8.23	.16	.033	.030	.074	.076
14.7	34.1	.13	.030	.015	.080	.084
14.6	77.2	.12	.026	.0093	.080	.083
4358 Å., 28 ± 3°						
3.63	141	0.012	0.0028	0.00019	0.010	0.011
10.4	168	.016	.0038	.00039	.013	.013
15.4	14.0	.0011	.00017	.00024	.00056	.00062
15.1	37.0	.0030	.00058	.00034	.0019	.0021
15.3	292	.017	.0038	.00048	.014	.016
15.4	428	.026	.0056	.00049	.022	.025
3650 Å., 28 ± 3°						
3.62	21.3	0.019	0.0011	0.00032	0.036	0.037
10.3	16.5	.019	.0018	.00073	.025	.026
12.8	20.4	.016	.0019	.00078	.018	.018
15.3	21.0	.017	.0020	.0011	.017	.019
15.1	65.5	.023	.0030	.00091	.025	.026

Table I presents data selected to emphasize certain points which will be discussed in some detail.[11]

It should be noted particularly that quantum yields are dependent on pressure, under some conditions on intensity, and on wave length. This means that reproducibility from one laboratory to another will be difficult to attain since actual values will depend on the nature of the light source and the way in which monochromatic light is obtained. Nevertheless the trends upon which the discussion of mechanism are based are real and the conclusions are almost entirely independent of the actual numerical values of the quantum yields.

Discussion

It is most convenient to discuss the primary process in terms of the mechanism proposed by Blacet and Bell.[3e,f] This mechanism, with the addition of reaction 2, is embodied in the following equations

$$(CH_3CO)_2 + h\nu = 2\alpha CH_3CO^{\pm} + (2 - 2\alpha)CH_3CO \qquad \phi I_a \quad (1)$$

$$CH_3CO^{\pm} = CO + CH_3 \qquad 2\alpha\phi I_a \quad (2)$$

$$CH_3CO = CO + CH_3 \qquad k_3(CH_3CO) \quad (3)$$

$$CH_3 + CH_3 = C_2H_6 \qquad k_4(CH_3)^2 \quad (4)$$

$$CH_3 + (CH_3CO)_2 = CH_4 + CH_2COCOCH_3 \qquad k_5(CH_3)(B) \quad (5)$$

$$= CH_3COCH_3 + CH_3CO \qquad k_6(CH_3)(B) \quad (6)$$

$$CH_3 + CH_3CO = CH_3COCH_3 \qquad k_7(CH_3)(CH_3CO) \quad (7)$$

$$CH_3 + CH_2COCOCH_3 = CH_3CH_2COCOCH_3 \qquad k_8(CH_3)(X) \quad (8)$$

$$CH_2COCOCH_3 = CH_2CO + CH_3CO \quad k_9(X) \quad (9)$$

$$2CH_3CO = (CH_3CO)_2 \quad k_{10}(CH_3CO)^2 \quad (10)$$

Reactions 5 and 6 have appreciable activation energies and will be unimportant at room temperature except at low intensities. Under low temperature conditions the main over-all reactions will be

$$CH_3COCOCH_3 = C_2H_6 + 2CO \qquad (11)$$

$$= CH_3COCH_3 + CO \qquad (12)$$

In the present experiments CO/C_2H_6 is always greater than 2 and hence reaction 12 must occur to an appreciable extent. Acetone may be formed either by (6) or by (7). From the data of Blacet and Bell it can be shown that (6) and (5) have com-

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(11) Material supplementary to this article has been deposited as Document Number 4409 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the Document number and by remitting $1.25 for photoprints or $1.25 for 35 mm. microfilm in advance by check or money order payable to: Chief, Photoduplication Service, Library of Congress.

parable rates so that a low methane yield means in general a low acetone yield by reaction 6.

The chain stopping steps are (4), (7), (8) and (10). The rate of (4) is measured directly by the rate of ethane formation since no other step for forming this gas is postulated. The rate of (8) may not exceed the rate of methane formation and may be zero if (9) goes to completion. Ways of estimating the rates of (7) and (10) must be found if the primary quantum yield is to be calculated from the data.

The value of k_7^2/k_4k_{10} has been estimated to be 11 at room temperature.[12] From the mechanism the primary quantum yield may be calculated from the following equations

$$\phi = \Phi_{CO} - \Phi_{C_2H_6} - (1 + k_6/k_5)\Phi_{CH_4} + k_{10}(CH_3CO)^2/I_a \qquad (13)$$

$$\phi = \Phi_{CO} - \Phi_{C_2H_6} - (1 + k_6/k_5)\Phi_{CH_4} + \frac{[\Phi_{CO} - 2\Phi_{C_2H_6} - (2 + k_6/k_5)\Phi_{CH_4}]^2}{11\ \Phi_{C_2H_6}} \qquad (14)$$

where ϕ is the number of biacetyl molecules dissociated per quantum absorbed. If all $CH_2COCOCH_3$ radicals dissociate by (9) the 2 should be replaced by 1 in the parenthetical expression with k_6/k_5 in the last term. It should be noted that equations 13 and 14 do not depend on α.

Use may also be made of $k_3{}^2/k_{10}$[12]

$$\phi = \Phi_{CO} - \Phi_{C_2H_6} - (1 + k_6/k_5)\Phi_{CH_4} + 1.1 \times 10^{-12}I_a(\Phi_{CO} - 2\alpha\phi)^2 \qquad (15)$$

Equation 15 may be used only at room temperature where $k_3{}^2/k_{10}$ has been estimated.

The values of k_6/k_5 can be obtained at various temperatures from the data of Blacet and Bell. Equations 14 and 15 magnify errors in the quantum yields but trends in ϕ should be significant. If ϕ, as calculated from (14), is substituted in (15), α may be calculated. The validity of these methods is best indicated from results at 2700 Å. at room temperature as shown in Table II.

TABLE II

CALCULATED VALUES OF PRIMARY QUANTUM YIELDS AND OF α, THE FRACTION OF INITIALLY FORMED ACETYL RADICALS WHICH DISSOCIATE IMMEDIATELY

2700 Å., 28°, 47 mm.

I_a, quant./ml./sec. × 10^{-12}	Φ_{CO}	ϕ Eq. 14	α
0.51	0.54	0.33	0.52
0.99	.44	.30	.49
2.9	.40	.31	.58
4.2	.39	.29	.54
	Av.	0.31	0.53

One run was made by Blacet and Bell under approximately the same conditions with the following results: $\Phi_{CO} = 0.55$; $\phi = 0.39$; $\alpha = 0.62$. These authors used a different light source and a different method of obtaining monochromatic radiation from that used in the present work. Since quantum yields vary with wave length and may vary with pressure, exact checks with present work would not be expected.

The constancy of ϕ and of α over a ten-fold variation in I_a indicates the following: (a) The values of $k_3{}^2/k_{10}$ and of $k_7{}^2/k_4k_{10}$ as obtained from the work on acetone[12] are mutually consistent within errors of this work; (b) One of the CH_3CO radicals produced in the primary dissociation of biacetyl at 2700 dissociates immediately due to energy retained from the primary process. This is equivalent to saying that the primary dissociation yields $CH_3 + CH_3COCO$ and that the latter radical dissociates immediately into $CH_3CO + CO$.

The constants k_7, k_4 and k_{10} are all for association reactions of radicals and hence should vary little with temperature. Equation 14 may be used, therefore, to a first approximation to calculate primary quantum yields at other temperatures. The same is not true of (15) since k_3 must have an activation energy at present not accurately known.

Blacet and Bell state that $\phi = \Phi_{C_2H_6}$ provided the mechanism is correct and provided also reactions (3) and (7) always go to completion. This should be nearly correct at temperatures near 100° but there are indications from material balance that the mechanism in (1) — (10) is not complete at higher temperatures. Also if $\alpha = 0.5$ and reaction 3 does not take place $\phi = \Phi_{CO}$. This is seen not to be strictly true even at room temperature although it may be nearly true at very high intensities.

It seems best to discuss the effect of conditions on the primary quantum yield at each wave length separately.

4358 Å.—Figure 1 shows a plot of primary quantum yield at 4358 Å. at room temperature against I_a. There is probably some effect of pressure on the yields so that scatter in the results would be expected. Nevertheless there is a strong indication that the primary yield increases with intensity at room temperature and that at constant pressure this relationship is almost linear.

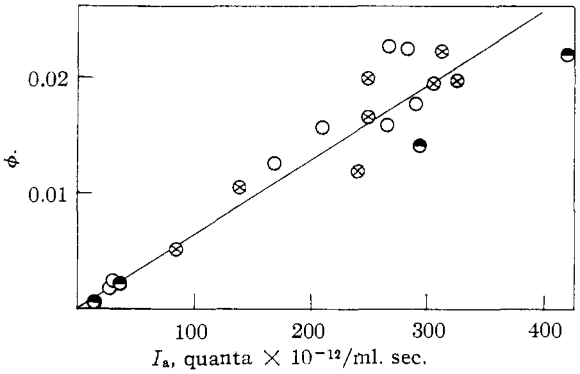

Fig. 1.—Primary decomposition yields at 4358 Å. *vs.* absorbed light intensity at 28°: ⊗, pressure range 10–60 mm.; ○, 0.31 mm.; ◓, 47 mm. Yields are calculated by equation 14 assuming $CH_2COCOCH_3$ combines with CH_3.

The fluorescence efficiency is about 0.14[3g] and the mean life is about 1.8 × 10^{-3} sec. at 25°.[3h,i,k] To a first approximation

$$(B^{**}) = \beta I_a/(5.6 \times 10^2 + k_{17}(B)) \qquad (16)$$

where β is the fraction of the absorbed quanta which

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[12] See ref. 6. Three errors occur in Table III, p. 796 of this reference. The value of this quantity should be 11 instead of 1.1 as given. Also $k_1/k_2{}^{1/2}$ (corresponding to $k_3/k_{10}{}^{1/2}$ in this article) should read 9.5 × 10^5 instead of 4.8 × 10^{-8}. This is because the intensity should be in the numerator instead of in the denominator of equation 37. Also $k_3k_6/k_4{}^2$ should read $k_3k_6/k_7{}^2$.

lead to the formation of the long lived state B**, 5.6 × 10^2 sec.$^{-1}$ is the sum of the rate constants for first-order decay of B** (including fluorescence by (18)), k_{17} is the constant for collisional deactivation by (17).

$$\mathrm{B^{**} + B = 2B} \qquad (17)$$

$$\mathrm{B^{**} = B} + h\nu \qquad (18)$$

k_{17} is evidently small[3m] and its maximum value is 7.2 × 10^{-17} ml. × (molecules sec.)$^{-1}$. k_{17}(B) may be neglected compared to 5.6 × 10^2.

If primary dissociation results from collision between two B** one finds at 303°K.

$$\phi = 0.2\beta^2 I_a \sigma^2 \qquad (19)$$

where σ^2 is the effective collision cross-section in square centimeters.

Two specific examples may be cited: (a) $\phi = 0.0018$, $\beta = 0.14$, $I_a = 37 \times 10^{12}$, $\sigma^2 = 130 \times 10^{-16}$ sq. cm., $\sigma = 11 \times 10^{-8}$ cm.; (b) $\phi = 0.020$, $\beta = 0.14$, $I_a = 326 \times 10^{12}$, $\sigma^2 = 160 \times 10^{-16}$, $\sigma = 13 \times 10^{-8}$ cm.

The diameters obtained in this way are large, but β may be larger than 0.14 since there may be other first-order processes for the disappearance of the state B** and 0.14 is the fluorescence efficiency. A lower limit for σ^2 is about 3 × 10^{-16} sq. cm.

Other ways to explain the intensity effect on the primary quantum yield have been considered. Direct dissociation may be followed by radical induced dissociation of activated or metastable molecules. If this process is accepted, it is difficult to visualize how a radical induced chain dissociation could occur. Direct dissociation at 4358 A. is unlikely because of the low energy per mole (66 kcal.). Radical recombination on the walls might reform biacetyl at low intensities and product formation might result from gas phase radical–radical reactions at high intensities. This latter possibility cannot be excluded but in general the pressure effect is not such as to support this idea strongly.

It is concluded tentatively that collisions between metastable biacetyl molecules of lifetime 1.8 × 10^{-3} second may account for the observed primary quantum yields at 4358 Å. at room temperature.

The grand average of α (21 runs) at 27 ± 3° is found to be 0.50 ± 0.07. There may be a trend toward lower values at low intensities but the significance of this trend is doubtful. Thus the nature of the primary dissociation seems to be similar to that at 2700 Å.

As the temperature is raised the quantum yields under otherwise identical conditions decrease, pass through a minimum at about 70° and then increase. Beyond the minimum the effect of intensity on the primary quantum yield is negligible so that the nature of the primary process has undergone a change. It is evident that at sufficiently low intensities there will not be a minimum in the primary yield. This point may be illustrated by the data in Table I at 100° at 4358 Å. where the calculated primary yield is 0.042 ± 0.01 with no trend apparent with either concentration or intensity.

The fluorescence mean life at 75° is about 1.3 × 10^{-3} sec.[3j] and the fluorescence efficiency is about 0.1. Thus one can show (equation 19) that the primary yield at 75° due to collision between two metastable molecules should be about 0.3 of the value at 30°. However β may not be measured by fluorescence efficiency so that the actual temperature effect may not be calculated with certainty. The data show that at 75° a ten-fold increase in intensity changes the primary yield by only 20 to 30% (Table I). There is also a small increase with increase in pressure. A plot of yield against intensity does not pass through the origin as it does approximately at 30°.

It is concluded that the main primary process follows one pattern at 30° and another at 100° but that at 75° both processes occur to measurable extents. Over this same temperature range there is a change in fluorescence behavior,[3m] *i.e.*, the fluorescence efficiency changes more rapidly above 100° than it does below and there is an activation energy of about 9000 cal. involved in the quenching process. On the other hand the increase in photochemical quantum yield with temperature above 75° does not occur at the expense of fluorescence and the increase involves an apparent activation energy of 20–30 kcal. Thus a thermally aided dissociation of B** does not seem to be involved.

The mechanism suggested to explain the fluorescence behavior at 4358 Å.[3m] may be extended to include the photochemical behavior. Since photochemical quantum yields are low, the initially formed upper state B′ may undergo some dissociation along with other competing processes such as deactivation and change to B**. The quantitative interpretation of the data in terms of a mechanism would have little meaning since the mechanism could not be shown to be unique. We suggest tentatively that the main dissociation at room temperature is by collision between two metastable molecules (presumably in the triplet state[3i]) whereas dissociation at higher temperatures occurs mainly from an upper vibration level of the state formed initially by the absorption of radiation (presumably the singlet state[3i]). This explanation may be correlated with the behavior at 3650 Å.

3650 Å.—The fluorescence efficiencies of both the short lived and the long lived fluorescences in biacetyl increase with increase in pressure at constant temperature when excited at 3650 Å.[3l] but not when excited at 4358 Å. It has been suggested[3e,g] that the initially formed state lies above a predissociation unit so that molecules may only fluoresce provided they lose energy by collision before they dissociate. Thus the primary photochemical quantum yield should decrease as the pressure increases.

One may modify slightly the mechanism suggested by Groh[3l] as

$$\mathrm{B} + h\nu = \mathrm{B}' \qquad I_a \qquad (20)$$

$$\mathrm{B}' = \mathrm{D} \qquad k_{21}(\mathrm{B}') \qquad (21)$$

$$\mathrm{B}' + \mathrm{B} = \mathrm{B}^* + \mathrm{B} \; k_{22}(\mathrm{B}')(\mathrm{B}) \qquad (22)$$

$$= \mathrm{B}^{**} + \mathrm{B} \; k_{23}(\mathrm{B}')(\mathrm{B}) \qquad (23)$$

where B* and B** are the two fluorescing species and D represents decomposition products. Other first-order steps parallel to (21) and second-order steps parallel to (22) and (23) may be added without changing the interpretation in essential respects. Hence

$$1/\phi = 1 + (k_{22} + k_{23})(B)/k_{21} \qquad (24)$$

Equation 24 neglects any dissociation which may result from interaction of two B**. The latter will cause some intensity dependence of the quantum yields at 3650 Å. at room temperature but will have no effect at 100°.

Figure 2 shows plots of $1/\phi$ *vs.* (B) at 30, 75 and 100°. In no case is the intercept unity and hence there must be one or more first-order processes competitive with (21). The intercept at 30° is more uncertain than the others due to the intensity effect. The intercepts are roughly the same at 75 and at 100°, and have the value of about 3. If the mechanism is correct about $^1/_3$ of the B′ molecules dissociate and the remainder disappear by some other first-order process at zero pressure. At 30° the intercept is somewhat higher.

The slopes of the lines in Fig. 2 decrease with increase in temperature so that (21) has a higher activation energy than the second-order steps for the disappearance of B′ by about 6 kcal.

The sum of the fluorescence quantum yield and three times the photochemical quantum yield is well below unity both at 75 and at 100°. Either B* or B** or both must disappear by processes other than fluorescence. Since the wave length of the fluorescence is apparently the same when excited by 4358 Å. as by 3650 Å., and since there is negligible self quenching at 4358 Å., these processes are presumably of the same order as the fluorescence, *i.e.*, first order. Deactivation to the ground state by second-order processes parallel to (22) and (23) is also possible.

From the mechanism it can be shown that

$$Q/\phi = a(B) \qquad (25)$$

where a is a rate constant related to the various rate constants and Q is the fluorescence efficiency, I_f/I_a. This relationship should be valid regardless of the number of steps parallel to (21) and (22) provided all dissociation occurs by (21) and provided also the rate of fluorescent emission is proportional to the sum of the rates (but not necessarily equal to the sum of the rates) of (22) and (23). Data to test (25) exist only at 30° where a plot of Q/ϕ *vs.* (B) gives a straight line which does not quite pass through the origin. Since some dissociation should result from collision between two B** the agreement with (25) is probably about as good as can be expected. Further tests of the mechanism would be advisable.

The value of α at 3650 Å. has been calculated. It depends to some extent on intensity and more markedly on pressure. At low pressures α is about 0.2 to 0.3 and reaches approximately 0.5 at higher pressures. The trend with intensity is less marked. These facts may possibly indicate that α for reaction 21 is lower than for that resulting from collision between two B** and may possibly depend on the vibration level of B′. It is definitely not possible to state, however, that α is zero for (21) and 0.5 for the other process.

The slopes of the lines in Fig. 2 at 75° and at 100° are 0.64 and 0.38 × 10^{-17} ml./molecule, respectively. If the activation energy difference between (21) and the various processes parallel to (22) is put at 6 kcal. (calculated from the slopes given above) and the pre-exponential factor given a *normal* value of 10^{13} sec.$^{-1}$, the collision diameters for (22) and its parallel reaction are found to be very large. If instead of 6 kcal. one uses 9 kcal. found from the fluorescence study at 4358 Å.,[3m] the collision diameters are reasonable.

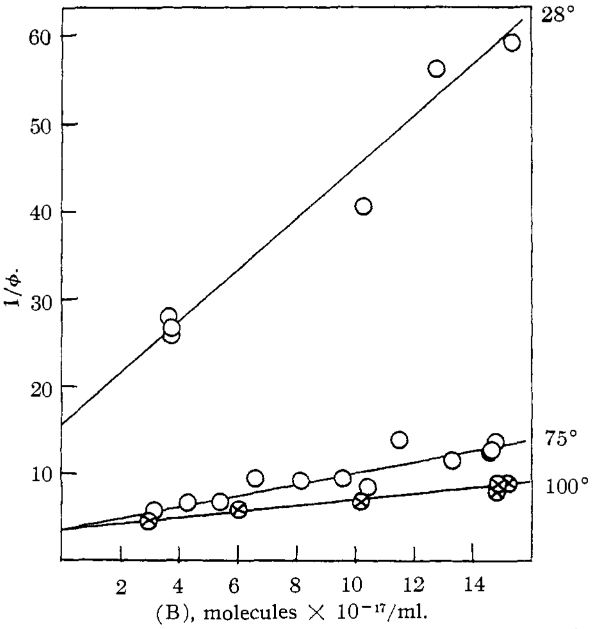

Fig. 2.—Inverse primary decomposition yield at 3650 Å. *vs.* biacetyl concentration at various temperatures. Yields are calculated by equation 14 assuming $CH_2COCOCH_3$ combines with CH_3.

If B′ loses 6 kcal. per mole it essentially becomes B**. If B** formed at 4358 Å. acquires 9 kcal. per mole it essentially becomes B′. Thus the phenomena at the two wave lengths may be related but the apparent activation energies need not agree exactly. The quenching of B** itself must be the same no matter how it is formed.

At present there is no satisfactory way of predicting the pre-exponential factors for reactions of the type of (21) so that further speculation about the meaning of these reactions is not useful. One may only say that the collisional process which deprives B′ of energy necessary for dissociation and hence which creates the fluorescing species has a very high probability and must occur on nearly every collision. This is in general agreement with what is known about the probability of redistribution of vibrational energy on collision.

Finally a word may be said about the primary process at 2700 Å. At this wave length Blacet and Bell[4f] find the primary quantum yield to be about 0.3, to be independent of temperature, and to be about the same in the presence and absence of iodine vapor. Nevertheless the primary yield is dependent on wave length in this general region of the spectrum. This fact coupled with the low primary yield means necessarily that a primary dissociation from an initially formed repulsive state does not occur. There must, therefore, be a time interval between absorption and dissociation with the result that vibrational energy may be lost. One would expect the yield to be pressure dependent and results found in this study show this to be the case. Blacet and Bell worked at only one pressure. The lack of dependence of primary yield on temperature is difficult to explain and further work at this wave length might prove to be of interest.

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The Metathetical Reactions of Methyl Radicals with Ethane, Dimethyl Ether, Acetone and Propylene[1]

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RECEIVED OCTOBER 27, 1954

The reactions of methyl radicals with shielded carbon atoms, oxygen atoms, carbonyl carbon atoms, and with carbon-carbon doubly bonded carbon atoms in organic molecules have been investigated experimentally. CD_3 radicals, produced in the thermal decomposition of CD_3CDO, were allowed to react with CH_3CH_3, CH_3OCH_3, CH_3COCH_3 and $CH_3CH{=}CH_2$. The CD_3–CH_3 exchange reactions with the first three compounds occur to the extent of less than one part in 1500, 2500 and 90, respectively, as compared with H-atom abstraction reactions. The CD_3-CH_3 exchange reaction with propylene could not be detected with high precision and seems to occur to the extent of about one part in ten as compared with H-atom abstraction.

Introduction

Some years ago Rice and Teller[3] considered the question of elementary reactions between radicals and molecules and concluded that the most probable reaction would be the removal of a hydrogen atom from an organic molecule by a free radical. They concluded that the attack on exposed negative atoms, such as chlorine, oxygen or nitrogen, having at least one pair of unshared electrons is unlikely as compared with removal of hydrogen atoms; they also concluded that the attack on a doubly or triply bonded carbon atom is entirely possible. The reaction least likely to occur would be the reaction between a free radical and carbon atom having all four valences joined to four univalent atoms or groups.

Experimentally, Rice, Walters and Ruoff[4] have concluded that the reactions

$$CH_3 + CH_3OCH_2CH_3 \longrightarrow CH_3OCH_3 + CH_3CH_2 \quad (1)$$

$$CH_3 + CH_3CH_2CH_2NH_2 \longrightarrow CH_3NH_2 + CH_3CH_2CH_2 \quad (2)$$

could be neglected in the thermal decomposition of methyl ethyl ether and n-propylamine since CH_3OCH_3 or CH_3NH_2 were not detected in the products. Franklin and Shepherd[5] have concluded that when methyl radicals attack isopropyl iodide 0.05-1.5% of the methyl radicals enter the reaction

$$CH_3 + i\text{-}C_3H_7I \longrightarrow C_4H_{10} + I \quad (3)$$

and that

$$CH_3 + i\text{-}C_3H_7I \longrightarrow CH_3I + i\text{-}C_3H_7 \quad (4)$$

might be possible since trace quantities of CH_3I were detected in the products.

Two reactions in which a methyl radical extracts a radical from a molecule have been postulated[6] in the photochemical decomposition of dimethylmercury[7] and biacetyl.[8]

$$CH_3 + CH_3HgCH_3 \longrightarrow CH_3CH_3 + Hg + CH_3 \quad (5)$$

$$CH_3 + CH_3COCOCH_3 \longrightarrow CH_3COCH_3 + CH_3CO \quad (6)$$

Recently, however, Rebbert and Steacie, and Holroyd and Noyes[9] have suggested that (5) probably does not take place.

Since this matter is extremely important in the study of elementary reactions,[10] an attempt has been made to obtain direct experimental evidence of the following types of reactions.

Attack on a shielded carbon atom

$$CD_3 + CH_3CH_3 \longrightarrow CD_3CH_3 + CH_3 \quad (7)$$

$$CH_3 + CD_3CD_3 \longrightarrow CH_3CD_3 + CD_3 \quad (8)$$

Attack on an exposed oxygen atom

$$CD_3 + CH_3OCH_3 \longrightarrow CD_3OCH_3 + CH_3 \quad (9)$$

Attack on a carbonyl carbon atom

$$CD_3 + CH_3COCH_3 \longrightarrow CD_3COCH_3 + CH_3 \quad (10)$$

Attack on a carbon–carbon doubly bonded carbon atom

$$CD_3 + CH_3CH{=}CH_2 \longrightarrow CD_3CH{=}CH_2 + CH_3 \quad (11)$$

These reactions have been studied in the thermal decomposition of the mixtures CD_3CDO–CH_3CH_3, CH_3COCH_3–CD_3CD_3, CD_3CDO–CH_3OCH_3, CD_3CDO–CH_3COCH_3, or CD_3CDO–$CH_3CH{=}CH_2$. Highly precise determination of most of the products of 7 to 11 is made possible by mass spectrometry.

Experimental

The pyrolytic apparatus and mass spectrometer have been described previously.[11] The heavy ethane was a mixture of 97.7% C_2D_6 and 2.3% C_2D_5H and the C_2H_6 was Phillips Research Grade gas 99.3% pure. The CD_3CDO was sup-

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(1) This work was supported by the United States Air Force under Contract No. AF-18(600)-64 monitored by the Office of Scientific Research.

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