of which disproportionation with other radicals is a very important source of major products. Another reaction of CH_3O is the abstraction of a hydrogen atom from CH_2O to give HCO radicals and CH_3OH. The HCO radicals then add O_2, the resulting performate radical passes to the formate radical. The formate radical disproportionates with the CH_3O radical yielding CO_2 and CH_3OH most of the time, but HCOOH and CH_2O occasionally.

The detailed reactions are given in the text and the ratios of rate constants are summarized in Table IX.

TABLE IX

SUMMARY OF RATE CONSTANT DATA

Rate constant ratio	Reference	Units	Av. value
k_f/k_g	Eq. 15	None	9.3 ± 0.6
$k_i^2/k_f k_c$	Eq. 19 and Fig. 6	$Mm.^{-1}$	0.007
$k_i^2/k_f k_c$	Eq. 19 and Fig. 6	Cc./mole	1.2×10^5
α_i	Eq. 19 and Fig. 6	None	0.055
α_b	Eq. 18 and Fig. 5	None	0.06
$k_h/k_f k_e^{1/2}$	Eq. 16 and Fig. 4	None	0.14 (CH_3I)
$k_h/k_f k_e^{1/2}$	Eq. 16 and Fig. 4	None	0.16 (C_2H_5I)
$k_v/k_f^{1/2}$	Eq. 16 and Fig. 4	$(Mm.\text{-}sec.)^{-1/2}$	1.44×10^{-4} (CH_3I)
$k_v/k_f^{1/2}$	Eq. 16 and Fig. 4	$(Mm.\text{-}sec.)^{-1/2}$	3×10^{-4} (C_2H_5I)
$k_v/k_f^{1/2}$	Eq. 16 and Fig. 4	$(Cc./mole\text{-}sec.)^{1/2}$	0.59 (CH_3I)
$k_v/k_f^{1/2}$	Eq. 16 and Fig. 4	$(Cc./mole\text{-}sec.)^{1/2}$	1.2 (C_2H_5I)
k_b/k_q	Eq. 18 and Fig. 5	$Mm.^{-1}$	5
k_b/k_q	Eq. 18 and Fig. 5	Cc./mole	1.0×10^8
k_l	Dark decay	$Sec.^{-1}$	$5 \pm 1 \times 10^{-3}$
k_m	Dark decay	$Sec.^{-1}$	$18 \pm 6 \times 10^{-3}$

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Energy Exchange in the 3-Methyl-2-butanone–biacetyl System at 3130 Å.

BY DAVID S. WEIR[1]

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The energy exchange taking place in the 3-methyl-2-butanone–biacetyl system has been studied at 3130 Å. 3-Methyl-2-butanone emits in the same region as acetone and 3-pentanone, and pressure and temperature dependence indicate that the emission is almost certainly composed of both singlet and triplet components. When excited by 3130 Å. radiation, a mixture of 3-methyl-2-butanone and biacetyl shows a very strong green biacetyl emission with maxima at 5120, 5600 and 6000 Å., indicating that an energy transfer mechanism between 3-methyl-2-butanone and biacetyl is important. A preliminary study of the effect of biacetyl pressure on this biacetyl emission suggests that two energy transfer steps are important: one involving triplet state ketone and biacetyl, as it is found in acetone and 3-pentanone, and the other involving singlet state ketone and biacetyl, previously considered unimportant in acetone and 3-pentanone.

The energy exchange taking place in the 3-methyl-2-butanone–biacetyl system has been studied at 3130 Å.

Eastman Kodak Co. methyl isopropyl ketone was used. The ketone was fractionated on a spinning band column and a middle fraction stored over Drierite for several days. The fraction was thoroughly degassed at Dry-Ice temperature in a vacuum line, and the middle fraction retained from a bulb-to-bulb distillation. Vapor phase chromatography gave impurities of less than 1%. Eastman Kodak Co. white-label biacetyl was dried over Drierite, degassed and fractionated in a bulb-to-bulb vacuum distillation. The purity was confirmed by vapor phase chromatography.

The experimental arrangement used for the light emission studies was similar to that used by Weir.[2] Light emissions were photographed on a Hilger quartz prism spectrograph using Eastman Kodak Co. 103-0 plates for the 3-methyl-2-butanone emission and 103-D plates for the excited biacetyl emission. Reflected incident light was removed by a Pyrex filter. The intensity of the biacetyl emission was measured on an R.C.A. WV-84A direct current microammeter connected to an R.C.A. 1P 21 photomultiplier tube. A Corning 3384 filter removed all emission below 5000 Å.

A conventional vacuum line was used.

3-Methyl-2-butanone emits light from about 3500 to about 4700 Å. when excited by 3130 Å. radiation. The emission, although more intense than the very weak emission produced from 3-pentanone, is weak and diffuse, requiring exposures of the order of 22 hours to produce a darkening of the photographic plate. The intensity of the emission is increased by an increase in ketone pressure and decreased 25% when the temperature is raised from 28 to 70°. The spectrum is unaffected by pressure, but the effect of temperature is difficult to assess due to the low intensity of the emission at 70°. The effect of added oxygen was inconclusive due once again to the weakness of the emission and also the restriction of O_2 pressures to the range below 4.0 mm., to avoid polymerization. As would be expected, very small amounts of biacetyl are formed during the photolysis of the 3-methyl-2-butanone and over long exposures at 28° a very weak biacetyl emission consisting of three bands with maxima at 5120, 5600 and 6000 Å. can be detected. The biacetyl emission is absent at 70°. The energy exchange between biacetyl and 3-methyl-2-butanone was confirmed by adding 5.6 mm. of biacetyl to 25 mm. of 3-methyl-2-butanone and photographing the very pronounced biacetyl emission. Because of the low intensity of the 3-methyl-2-butanone emission it was impossible to determine whether the addition of biacetyl produced any effect on the intensity or spectrum of this emission.

The effect of biacetyl on the phosphorescence of biacetyl in a 3-methyl-2-butanone–biacetyl mixture is shown in Table I, where the effect is compared to that obtained from the 3-pentanone–biacetyl system.

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[2] D. S. Weir, *J. Am. Chem. Soc.*, **83**, 2629 (1961).

TABLE I

EFFECT OF BIACETYL ON THE PHOSPHORESCENCE OF BIACETYL IN A MIXTURE OF BIACETYL AND 3-METHYL-2-BUTANONE AND BIACETYL AND 3-PENTANONE AT 28° AND 3130 Å.

Biacetyl press., mm.	Biacetyl phosphorescence, μamp. In 25 mm. of 3-methyl-2-butanone	In 25 mm. of 3-pentanone
0.0	0.00	0.00
.3	.35	8.65
.6	.58	11.65
.9	.75	...
1.2	.95	14.50
1.5	1.10	...
1.8	1.20	15.00
2.1	1.30	...
2.4	1.40	15.00
2.7	1.50	
3.0	1.60	
3.6	1.85	
4.2	2.05	
4.8	2.25	

3-Methyl-2-butanone emits in the same region as acetone[3-7] and 3-pentanone.[2] The emission is much weaker than that obtained from acetone, although it is slightly stronger than the corresponding 3-pentanone emission. The pressure dependence suggests that the emission arises from a low vibrational level of an upper excited state and the emission is almost certainly composed of both singlet and triplet components. The effect of temperature indicates the removal through decomposition of the longer lived component, *i.e.*, the triplet state, although results obtained from 3-pentanone[2] suggest that the singlet state decomposition can also be increased by an increase in temperature.

When excited by 3130 Å. radiation, a mixture of 3-methyl-2-butanone and biacetyl shows a very strong green emission with maxima at 5120, 5600 and 6000 Å. This is undoubtedly the biacetyl emission indicating that the energy transfer mechanism

$$K_0^3 + B = B_0^3 + K \qquad (1)$$

followed by

$$B_0^3 = B + h\nu_{B_0^3} \qquad (2)$$

(where K_0^3 and K are 3-methyl-2-butanone molecules in low vibrational levels of the upper triplet state and normal state, respectively, and B_0^3 and B are biacetyl molecules in corresponding states, respectively), as suggested by Okabe and Noyes,[8] is important. A similar situation has been shown to exist in acetone[9] and 3-pentanone.[2]

The possibility of corresponding energy transfer by the excited singlet state ketone molecules has been considered small by Heicklen[10] for the acetone–biacetyl system and by Okabe and Noyes[8] for the biacetyl case. Such energy transfer could be neither proved nor disproved in the 3-pentanone–biacetyl system.[2] A preliminary study of the effect of biacetyl on the biacetyl emission from mixtures of biacetyl and 3-methyl-2-butanone shows that a different mechanism is involved compared to that encountered in 3-pentanone–biacetyl system (*cf.* Table I). In 3-pentanone, addition of biacetyl produced an initial increase in the biacetyl phosphorescence. At a biacetyl pressure of about 1.2 mm. the increase leveled off and a constant emission was obtained with increasing biacetyl pressure. This was interpreted as an indication of the removal of triplet state-3-pentanone by the biacetyl according to step 1, followed by step 2. At 1.2 mm. biacetyl sufficient biacetyl was present to remove completely the triplet state 3-pentanone and further increase in phosphorescence therefore did not occur. In 3-methyl-2-butanone the intensity of the biacetyl emission increases with biacetyl pressure in similar manner to the 3-pentanone system, the rate of increase decreasing with increasing biacetyl pressure. At about 1.2 mm. pressure of biacetyl, however, the biacetyl phosphorescence continues to increase linearly with biacetyl pressure. Such an effect may be explained by including steps 3 and 4 in the mechanism, whereby energy is transferred

$$K_0^1 + B = B_0^1 + K \qquad (3)$$

$$B_0^1 = B_0^3 \qquad (4)$$

(where K_0^1 and B_0^1 refer to 3-methyl-2-butanone and biacetyl, respectively, in the lower vibrational levels of the upper singlet state), from 3-methyl-2-butanone in an upper excited singlet state, to normal biacetyl, forming biacetyl molecules in an upper singlet state which subsequently undergo rapid conversion to the triplet state as proposed by Okabe and Noyes.[8] At low biacetyl pressures, therefore, the increase in biacetyl phosphorescence arises from triplet state biacetyl formed according to steps 1 and 3 followed by step 4. At about 1.2 mm. pressure biacetyl, sufficient biacetyl is present to remove completely the triplet state 3-methyl-2-butanone and subsequent increase in phosphorescence arises solely from steps 3 followed by step 4.

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