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

The Photolysis of Ketene at Low Pressure[1]

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Apparent quantum yields of carbon monoxide and of ethylene have been determined at wave length 3650 Å. as functions of temperature and of concentration of ketene. At the lowest concentrations studied the yield of ethylene decreases, probably because of heterogeneous disappearance of methylene radicals. Apparent quantum yields of carbon monoxide, based on a Beer's law extrapolation, are constant at concentrations below 5×10^{-5} mole/liter. The significance of this constancy is discussed in terms of a detailed mechanism including an internal conversion process.

Introduction

At 3650 Å. wave length, electronically excited ketene molecules are formed which can undergo dissociation, collisional deactivation or internal conversion.[3] The quantum yields of the products, carbon monoxide and ethylene, are small and their reciprocals are linear functions of the concentration of ketene. The primary quantum yield, equal to half the quantum yield of carbon monoxide,[3,4] extrapolates to 0.062 at zero concentration. Provided that the extrapolation to zero concentration is valid, there must be an internal conversion process with the same order in ketene concentration as the dissociation process.

The question arises as to the detailed nature of the internal conversion process. A reasonable explanation is that a radiationless transition occurs from the excited electronic state to an upper vibration level of the ground electronic state, followed by rapid collisional deactivation. The present work explores this reaction at low concentrations of ketene. If internal conversion does occur by these reactions, the primary quantum yield should increase rapidly at low concentrations and tend toward unity at zero concentration.

Experimental

The preparation of materials and method of analysis of products have been described previously.[3,5] A British Thomson–Houston Hg lamp ME/D 250 watt, operated on 220 v.a.c., was focussed with a quartz lens to a nearly parallel beam. A Corning filter #7380 between the lens and reaction cell transmitted only wave lengths longer than 3400 Å. Since ketene does not absorb appreciably at wave lengths longer than 3700 Å., the radiation absorbed was essentially from the Hg lines at 3650 Å.

A 22-liter spherical Pyrex flask was enclosed in an air oven. The light beam, 6 cm. in diameter, traversed the center of this flask. The radiation leaving the reaction cell passed through a Corning filter #5860 and was focussed either on an RCA #935 phototube or on a uranyl oxalate actinometer. A 2 stage Hg diffusion pump was connected by 15 mm. tubing to the reaction cell to evacuate the cell and to collect the products for analysis. All analyses were checked by determinations on synthetic mixtures.

Results

Apparent quantum yields of carbon monoxide at room temperature are given in Table I. The absorbed intensity was calculated from the measured incident intensity with Beer's law using the absorption coefficient determined at a high concentration. The quantum yields obtained in this manner are called apparent quantum yields. This procedure proved necessary as the fraction of radiation absorbed was too small to be measured directly. The apparent quantum yields are expected to be somewhat higher than the absolute quantum yields in the low concentration region since the spectrum of ketene near 3650 Å. is discontinuous.[6] This effect is found at high concentrations: experimental values of the molar extinction coefficient at 5.4×10^{-3} and 1.9×10^{-3} moles/liter were 2.14 and 3.82 liter/mole cm., respectively. However, at sufficiently low concentrations that absorption is far from complete at the centers of the lines in the spectrum, the apparent quantum yields will be proportional to the absolute quantum yields.

TABLE I

PHOTOLYSIS PRODUCTS OF KETENE AT 3650 Å. AND AT 27°

Ketene, moles/l. × 10^6	$R_{CO}/R_{C_2H_4}$	Φ_{CO}(apparent)	Φ_{CO}(extrap.)[b]
0.88[a]	12.3	0.54	0.062
1.02	5.9	..	...
1.47	5.7	..	...
2.04[a]	8.9	.54	.062
3.81[a]	10.8	.53	.062
3.95	5.5	..	...
4.34[a]	50	.56	.062
6.24[a]	100	.55	.062
25.9	3.4	..	...
47.3	2.8	.56	.056
507	3.1	.22	.033
1085	2.5	..	...
1640	2.3	..	...

[a] Runs prior to which the cell had been open to air and not thoroughly outgassed. [b] From ref. 3.

The ratio of the yield of carbon monoxide to that of ethylene was found to be a function of ketene concentration, as shown in Table I. The data show considerable scatter and a strong dependence on the condition of the cell walls. After the cell had been exposed to air then evacuated (but not subjected to high temperature outgassing), a definite reduction in the ethylene yields was noted. In some of these runs, essentially no ethylene could be detected.

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The rates of formation of products were studied at four temperatures and at a concentration of 1.5 × 10^{-6} mole/liter. The data are given in Table II. One run in this series at 3130 Å. demonstrates that the high ratio of carbon monoxide to ethylene is independent of the wave length absorbed, within experimental error.

TABLE II

EFFECT OF TEMPERATURE ON THE RATE OF PRODUCT FORMATION IN THE PHOTOLYSIS OF KETENE AT 3650 Å.

Ketene, moles/l. × 10^{-6}	t, °C.	$R_{CO}/R_{C_2H_4}$	Φ_{CO}(apparent)
1.47	27	5.7	0.54
1.49	70	3.3	1.02
1.51	106	3.6	1.73
1.53	154	2.9	2.50
1.56 (3130 Å.)	70	4.1	..

Discussion

The mechanism for a photochemical reaction that proceeds *via* excited molecules can be represented by the following series of reactions (using the notation of ref. 4). For simplicity, only one upper electronic state is considered, although there may be more involved, as in biacetyl.[4]

$$X + h\nu = Y_n \tag{1}$$

$$Y_n + M = X + M \tag{2}$$

$$Y_n = D \tag{3}$$

$$Y_n = X_m \tag{4}$$

$$X_m = Y_n \tag{5}$$

$$X_m = X_i \tag{6}$$

$$X_i = X_m \tag{7}$$

$$X_i + M = X + M \tag{8}$$

X is a molecule (*e.g.*, ketene) in its ground electronic state in thermal equilibrium with its surroundings; Y_n is a molecule in an upper vibronic state reached by absorption of radiation; D represents the dissociation products (in this case, carbon monoxide and methylene radicals); M is a molecule capable of degrading vibrational energy by collision. X_i represents those molecules in high vibration levels of the ground electronic state having the same total energy as Y_n. There will be many degenerate states corresponding to X_i, but only a few, designated by X_m, will have a configuration such that a radiationless transition to Y_n has a high probability. A molecule X_i will spend only a small fraction of its lifetime in the configuration X_m. X_m is the state formed when a molecule Y_n makes a transition to the ground electronic state (reaction 4). Internal conversion is considered to have occurred after reaction 8 has removed sufficient energy from X_m to prevent its return to Y_n.

The primary quantum yield, ϕ, calculated from this mechanism is the same as that derived from a simpler mechanism,[3] as long as the concentration is high enough that $k_8(M) >> k_7$. In the low concentration region where this relationship is no longer valid, ϕ should increase with decreasing concentration and, in the limit of zero concentration, should be unity. Since the apparent quantum yield of carbon monoxide found experimentally is independent of concentration down to 10^{-6} mole/liter, it follows that the rate constant k_7 must be small compared with $k_8(M)$. Thus all excited ketene molecules that make the transition from Y_n to X_m (reaction 4) are subsequently deactivated by collision even at the lowest concentration studied here. If the assumption of incomplete absorption of radiation at the centers of the lines in the spectrum were not valid even at these low concentrations, the constancy of the apparent quantum yields would mean that the primary quantum yield decreases with decreasing concentration of ketene, a result that does not appear to be reasonable.

It should be noted that reaction 9 cannot be included in the mechanism. Thus, dissociation must

$$X_i = D \tag{9}$$

take place either directly from Y_n or from another electronic state to which Y_n goes by a radiationless transition.

The data on the decrease of the ethylene yield at low concentrations are not amenable to quantitative treatment. The large scatter in the data is almost certainly due to the heterogeneous character of the reaction. A competition between reactions 10 and 11

$$CH_2 + CH_2CO = C_2H_4 + CO \tag{10}$$

$$CH_2 \text{ (+ wall)} = \text{Product (not } C_2H_4) \tag{11}$$

leads to a qualitative description of the results. The accommodation coefficient at the walls seems to increase when water or one of its reaction products with ketene is adsorbed on the walls of the reaction cell. Since the accommodation coefficients are not known even in order of magnitude, it is not possible to obtain information about the rate of reaction 10 from these data.

The apparent quantum yields of carbon monoxide at the four temperatures studied give a straight line when plotted in the Arrhenius form, corresponding to an activation energy of about 3 kcal. This activation energy is due in part to a small change in the absorption coefficient with temperature. However, the result agrees well with that found by Strachan and Noyes[3] and corresponds approximately to $E_3 - E_4$.

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