159. *The Influence of Inert Gases on the Photodecomposition of Gaseous Acetone.*

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A study has been made of the influence of the inert gases carbon dioxide and nitrogen at pressures near to atmospheric on the photodecomposition of gaseous acetone at room temperatures in light of wave-length 2400—3100 A. The yield of carbon monoxide was found to be increased, no detectable amounts of diacetyl were formed, and the ratio C_2H_6/CO approached unity. Reasons are given for this change in behaviour of the photodecomposing acetone.

The photodecomposition of gaseous acetone has been the subject of many investigations. The main products are ethane, carbon monoxide, and diacetyl, with increasing amounts of methane as the temperature is raised (Damon and Daniels, *J. Amer. Chem. Soc.*, 1933, **55**, 2363; Norrish, Crone, and Saltmarsh, J., 1934, 1456; Barak and Style, *Nature*, 1935, **135**, 307; Spence and Wild, J., 1937, 352; 1941, 590; Herr and Noyes, *J. Amer. Chem. Soc.*, 1940, **62**, 2052). The different proportions of the products, and, in particular, the ratio C_2H_6/CO, depend very much on the wave-length of the light used, the intensity of the light, and the pressure of the acetone. The absorption spectrum of acetone is not an easy one to interpret, but definite regions have now been distinguished, and certain consequences to the molecule on absorption of light in these regions have been assumed (Baur and Rebmann, *Helv. Chim. Acta*, 1922, **5**, 828; Scheibe, Povenz, and Linstrom, *Z. physikal. Chem.*, 1933, *B*, **20**, 297; Noyes, Duncan, and Manning, *J. Chem. Physics*, 1934, **2**, 717; Norrish, Crone, and Saltmarsh, *loc. cit.*). The " banded " region in the neighbourhood of 3130 A. gives rise to excited molecules, as likewise does another banded region on the borderland of the quartz ultra-violet, 1800—1950 A. (Howe and Noyes, *J. Amer. Chem. Soc.*, 1936, **58**, 1404). Light absorbed in the " continuum " region, 2500—3000 A., breaks the molecule into radicals: $CH_3{\cdot}CO{\cdot}CH_3 + h\nu = CH_3 + CO{\cdot}CH_3$. The acetyl radical $CH_3{\cdot}CO$, however, is not very stable, and sometimes contains enough internal energy, on rearrangement, to break it up into CH_3 and CO. It may lose this energy by collision with other molecules, but at higher temperatures there is a greater probability of its acquiring more energy by collisions to make it again unstable. Low temperatures and high light intensities therefore favour the detection of this radical, which can combine with itself to give diacetyl: $2CH_3{\cdot}CO = (CH_3{\cdot}CO)_2$. A high value of the ratio C_2H_6/CO indicates the formation of relatively large amounts of diacetyl, and a low value small amounts. Ultimately, when C_2H_6/CO becomes unity, no diacetyl is formed.

It seems that the excited molecules formed in the 3130 A. region can also break up into CH_3 and $CO{\cdot}CH_3$, although not immediately, according to the assumptions of Spence and Wild (1941, *loc. cit.*). Diacetyl is therefore formed in this region as well as in the continuum. The over-all results obtained in the " banded " region are somewhat different from those in the " continuum," and rather different results are obtained again when " mixed light," *i.e.*, λλ 2500—3100 A., is used. These matters are not discussed here, but such of them are mentioned later as have a bearing on our discovery that in the presence of such inert gases as carbon dioxide and nitrogen at moderately high pressures, no detectable amounts of diacetyl are formed.

EXPERIMENTAL.

Acetone.—The acetone was purified by treatment with successive small quantities of potassium permanganate until no more brown coloration appeared. It was then kept over potassium carbonate, distilled, dried over calcium chloride, and fractionated, the portion of b. p. 56·0—56·1° being collected.

Carbon Dioxide.—The gas was prepared from marble and hydrochloric acid, passed over moist copper sulphate and through sulphuric acid. Quantities of carbon dioxide were collected in a glass vessel attached to the photochemical apparatus by freezing it in a vacuum, vaporising it, and again freezing it to remove traces of oxygen and nitrogen.

Nitrogen.—The nitrogen was obtained from a cylinder and passed through alkaline pyrogallol and sulphuric acid, and sometimes over red-hot copper, before admission to the apparatus, in order to remove traces of oxygen.

Apparatus.—The photochemical set-up differed in no way from the type usually employed, except that the cylindrical photo-cell of quartz, 6·5 cm. long by 3·5 cm. internal diameter, was attached to the main vacuum line by a long quartz tube (65 cm.) terminating in a quartz-to-glass joint. This was in place of a greaseless valve, which was unprocurable. The possibility of reaction between any radicals formed and the tap grease on this joint at this distance is very remote.

A mercury vapour lamp, of the Hanovia " Homesun " type, was used as a source of ultra-violet light.

The small quantities of carbon monoxide and ethane obtained during a run were estimated with the aid of a micro-gas analysis apparatus, similar to that described by Blacet and Leighton (*Ind. Eng. Chem. Anal.*, 1933, **5**, 272). All of the gas formed during a run was pumped off by a small Toepler pump, and a portion analysed for the C_2H_6/CO ratio. This procedure is necessary to recover all of the ethane, without which the ratio obtained would not be the correct one. The ethane was determined by explosion with oxygen, the water absorbed by a phosphoric oxide bead, and the carbon dioxide by a potassium hydroxide bead. The carbon monoxide was determined by absorption in a bead of silver oxide prepared as described by Blacet and Leighton (*loc. cit.*), dried in a partial vacuum, and highly compressed. After a run, the carbon monoxide and ethane were pumped off, and the condensable material was frozen out with freezing *iso*amylene (— 125°) or methanol (— 90°). When carbon dioxide was present, the greater part of it was absorbed by solid potassium hydroxide, the small, residual amount being taken up by a potassium hydroxide bead during the first stage of the gas analysis. The diacetyl was estimated in separate experiments by Vizern and Guillot's method (*Ann. Falsif.*, 1932, **25**, 459), which depends on its conversion into dimethylglyoxime and comparison of the red colour then produced by nickel sulphate with that from solutions of known diacetyl content. Results were probably accurate to within 10%.

DISCUSSION.

Some of our earlier experiments were concerned with finding out if the presence of a platinum-black-coated platinum gauze had any influence on the photodecomposition of acetone, but these were inconclusive, as the effects observed were not much outside the experimental error. When an inert gas such as nitrogen or carbon dioxide (without the gauze) was added to the acetone decomposing in light of the 2400—3130 A. region, however, very definite and reproducible results were obtained. In the experiments listed in Table I the acetone was illuminated by light of the same intensity for the same period (16 minutes) in each case. All the products of decomposition, except the carbon monoxide, were frozen out with liquid air.

The yield of carbon monoxide is increased by a factor of about 1·7. This suggests two possibilities: (1) an overall increase in the quantum yield of acetone decomposed, and (2) breakdown of the $CH_3{\cdot}CO$ radical, owing to its greater instability in the presence of gases of higher pressure. The second of these effects would manifest itself as a diminished yield of diacetyl.

TABLE I.

Temperature: 19—20°

Acetone, mm. Hg.	CO_2, mm. Hg.	CO formed, c.c.	Acetone, mm. Hg.	CO_2, mm. Hg.	CO formed, c.c.
150	0	0·020	150	620	0·036
,,	,,	0·019	,,	610	0·034
,,	,,	0·020		Unilluminated	
,,	600	0·034	,,	630	0·0005

In some fresh experiments diacetyl was tested for, not only in the condensate frozen out with liquid air after each run, but also in the reaction vessel itself (Table II).

TABLE II.

Temperature : 18—20°.

Added gas.	Pressure of added gas, mm.	Pressure of acetone, mm.	Diacetyl formed, mg.
—	—	150	2·0
—	—	155	2·2
—	—	140	2·0
CO_2	620	150	0
CO_2	590	150	0
N_2	600	150	0
,,	640	140	0
,,	640	150	0

If diacetyl is not formed under these conditions, or only formed in minute, undetectable amounts, the only analysable products of the photoreaction other than some polymerised material (which, however, is considered to arise from the diacetyl) will be carbon monoxide and ethane, the latter being formed from the union of two methyl radicals. (A small amount of methane is sometimes found, even at room temperature, owing to secondary reactions, such as $CH_3 + CH_3{\cdot}CO{\cdot}CH_3 = CH_4 + CH_2{\cdot}CO{\cdot}CH_3{\cdot}$.) The ratio C_2H_6/CO in the absence of diacetyl should be unity (see p. 589). The results of our micro-analyses confirm this (Table III), although it must be admitted that with the " mixed light " (2400—3130 A.) of high intensity the ratio C_2H_6/CO is not very high (1·25—1·40) in the absence of the inert gas.

TABLE III.

Temp.	22°	22°	21°	21°	22°	19°	24°	24°	18°	20°	21°	18°
Press. of acetone (mm.)	149	149	154	154	150	163	175	175	158	162	168	148
Press. of CO_2 (mm.) ...	0	0	0	0	0	0	540	540	620	590	580	610
C_2H_6/CO	1·25	1·34	1·25	1·35	1·40	1·32	0·88	0·92	0·98	1·13	1·09	0·94

Our explosion results, obtained with oxygen and the gas left after the absorption of the carbon monoxide, indicated that a small amount of methane may have been formed during the photolysis, but this in no way affects our general conclusions.

There are two ways in which the inert gas may act to prevent the formation of diacetyl : (1) by increasing the collision frequency of the acetyl radical with other molecules, thereby enabling it to acquire enough activation energy to dissociate into methyl and carbon monoxide. Gorin (*J. Chem. Physics*, 1939, **7**, 256) estimates that the energy required for this process is 17,000 cals. [in Spence and Wild's scheme for the photodissociation of acetone (1941, *loc. cit.*), the stability of $CH_3{\cdot}CO$ is shown to be pressure-dependent in the equation $CH_3{\cdot}CO + M = CH_3 + CO + M$]; (2) by hindering the diffusion of acetyl radicals to the walls of the reaction vessel, where they combine to give diacetyl : $2CH_3{\cdot}CO = CH_3{\cdot}CO{\cdot}CO{\cdot}CH_3$.

The increase in the quantum yield of carbon monoxide must be linked with this diacetyl factor, but it need not be attributed solely to this, and indeed, the presence of the inert gas may act adversely in preventing the breakdown of the excited acetone molecules found in the banded region, by assisting in their deactivation. The increase in the carbon monoxide yield may therefore be actually less than the expected amount due to this deactivation. The quantum yield for acetone deomposed will of course be increased, because destruction of the acetyl radical inhibits the back reaction $CH_3{\cdot}CO + CH_3 = CH_3{\cdot}CO{\cdot}CH_3$.

Let a and b be the concentrations of ethane and carbon monoxide, respectively, found in absence of inert gas, and x = increased concentration of the monoxide in presence of inert gas. Then, using our mean results for C_2H_6/CO ratios, we have : $a/b = 1{\cdot}32$, $(a + 0{\cdot}5x)/(b + x) = 1{\cdot}0$, whence $(b + x)/b = 1{\cdot}64$. Our experimental factor 1·7 expressing the increased yield of carbon monoxide is very close to this value, but more accurate experiments will be necessary to show whether or not the deactivation of excited acetone molecules by the inert gas has any considerable influence on the yield of carbon monoxide. Experiments were begun with only continuum light (~2537 A.), but have had to be interrupted.

Our results are to some extent comparable with those of Howe and Noyes (*loc. cit.*), who used inert gases in the 1800—1900 A. region. They found that the gases increased the quantum yield for acetone decomposed, but they were not concerned with the formation of diacetyl, and assumed that the inert gas assisted in breaking up the excited acetone molecules.

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