CCX.—*The Photolysis of Acetaldehyde and of Acetone.*

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IT was shown by Berthelot and Gaudechon (*Compt. rend.*, 1913, **156**, 68, 233) that acetaldehyde is partly polymerised in ultraviolet light and partly decomposed into methane and carbon monoxide; also (*ibid.*, 1910, **151**, 478) that acetone is decomposed into ethane and carbon monoxide. In aqueous solutions acetone is said to be photolysed to methane and acetic acid.

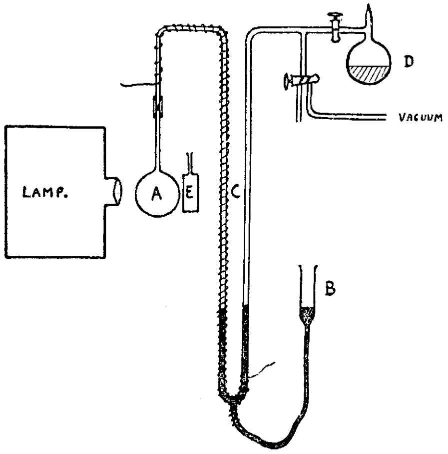
The following experiments were made to compare the number of molecules chemically changed with the number of molecules activated, *i.e.*, with the number of quanta absorbed. No work of this kind on gaseous aldehydes and ketones seems to have been done, although Volmar (*Compt. rend.*, 1924, **178**, 697), apparently without experimental evidence, assumed that these reactions obeyed the Einstein-Stark law.

Experiments with Acetaldehyde Vapour.

The apparatus is shown diagrammatically in the figure. A mercury vapour lamp made by the Thermal Syndicate was contained in a box fitted with quartz condensing lenses so that approximately parallel light fell on the fused quartz reaction bulb A, which was filled with acetaldehyde vapour by lowering the mercury reservoir B, evacuating with two mercury vapour pumps in series, and then connecting with the liquid aldehyde in D through the tap. The reservoir B was then raised so that mercury rose in the limbs of the U-tube C, and the tap on the right hand limb opened to the atmosphere. The amount of photochemical change was measured by pressure changes in the left hand limb, which was heated electrically to prevent condensation of liquid.

For the measurement of the energy of the ultra-violet light, use was made of the "ultra-violet radiometer" of Anderson and Robinson (*J. Amer. Chem. Soc.*, 1925, **47**, 718) which is based upon the decomposition of oxalic acid in uranyl sulphate solutions. There is a serious discrepancy in the results of different investigators of this reaction. Anderson and Robinson state that in ultra-violet light 1 molecule of oxalic acid is decomposed for every 25 quanta absorbed; Boll (*Compt. rend.*, 1913, **156**, 1891) states that 50 molecules of oxalic acid are decomposed for each quantum absorbed; whilst Büchi (*Z. physikal. Chem.*, 1924, **111**, 269) finds that the reaction obeys the Einstein-Stark law. We therefore made direct measurements of the photochemical efficiency of this reaction.

FIG. 1.



The mercury vapour lamp with quartz condensing lenses was set up with a 5 cm. water-filter, and the light passed through a stop on to a cell with fused-on ends of plane-polished quartz containing the uranyl sulphate ($0{\cdot}01M$) and oxalic acid ($0{\cdot}1N$) solutions. The oxalic acid decomposed was estimated with $N/20$-potassium permanganate solution, and the total energy of the light measured with a Moll thermopile calibrated against a Hefner lamp (Gerlach, *Physikal. Z.*, 1913, **14**, 577). The amount of light absorbed was obtained from the difference in readings of the galvanometer connected to the thermopile when the quartz cell contained water or the solution. The results were as follows :

Galvanometer readings (1 division = $1{\cdot}4 \times 10^{-4}$ cal./sec.) :
  Total energy of lamp falling on cell = 50 divisions.
  Quartz cell filled with water = 30·5 ,,
  ,, ,, ,, ,, solution = 17·5 ,,

Thus, cal. absorbed by solution per sec. = $2{\cdot}8 \times 10^{-3}$.
Taking the Hg line 3130 Å. as the mean wave-length absorbed, 1 gram-molecular quantum = 85,000 cal.; therefore the number of gram-molecular quanta absorbed per sec. = $3{\cdot}3 \times 10^{-8}$. In three experiments, each of 1 hour's exposure, the amount of oxalic

acid decomposed per second was 3·0, 3·35, and $3{\cdot}5 \times 10^{-8}$ g.-mol., respectively. From these results it appears that it may safely be assumed, in agreement with Büchi, that for each quantum of ultra-violet light absorbed one molecule of oxalic acid is decomposed.

The absorption of the aldehyde vapour was then measured by the difference in the photochemical change taking place in the uranyl sulphate–oxalic acid solution in the plane-walled quartz vessel E when the bulb A was empty and when it was filled with aldehyde vapour; also, by placing the vessel E in the place of A, the total amount of ultra-violet light could be measured.

Acetaldehyde undergoes two photochemical changes:

(1) Photolysis, $CH_3{\cdot}CHO = CH_4 + CO$.

(2) Polymerisation, $3CH_3{\cdot}CHO$ = paraldehyde + metaldehyde, etc.

The first series of measurements was made with a little liquid aldehyde in the bulb, *i.e.*, with saturated vapour, only the vapour being exposed to the light. If x molecules are changed according to reaction (1), the pressure change will be proportional to $2x$, the second reaction giving condensation products which do not affect the pressure appreciably. The results were:

Volume of reaction vessel = 125 c.c.

Pressure *increases* in cm. Hg after 1 hour's exposure. $= \begin{cases} 0{\cdot}59,\ 0{\cdot}665,\ 0{\cdot}55,\ 0{\cdot}685. \\ \text{Mean} = 0{\cdot}62. \end{cases}$

Thus, $2x = 125 \times 0{\cdot}62/3600 \times 76 \times 23400 = 1{\cdot}2 \times 10^{-8}$ g.-mol./sec. or $x = 0{\cdot}6 \times 10^{-8}$ g.-mol./sec.

A second series of experiments was made with unsaturated vapour; a diminution in pressure then took place showing that more molecules are polymerised than photolysed. If y is the number of molecules activated for the reaction

$$CH_3{\cdot}CHO \text{ (activated)} + 2CH_3{\cdot}CHO = \text{condensation products,}$$

the diminution in pressure is proportional to $(3y - x)$. The results were:

Pressure *decreases* in cm. Hg. after 1 hour's exposure. $= \begin{cases} 3{\cdot}5, 3{\cdot}9, 3{\cdot}3, 3{\cdot}8, 2{\cdot}8, 2{\cdot}4. \\ \text{Mean } 3{\cdot}5. \end{cases}$

Thus, $3y - x = 125 \times 3{\cdot}5/3600 \times 76 \times 23400 = 6{\cdot}85 \times 10^{-8}$ g.-mol./sec., whence $y = 2{\cdot}48 \times 10^{-8}$ g.-mol./sec.

Total number of g.-mols. activated per second for photolysis and polymerisation $= x + y = 3{\cdot}08 \times 10^{-8}$.

Number of gram-molecular quanta absorbed per second by aldehyde vapour (obtained from oxalic acid–uranyl sulphate solution titrations) $= 1{\cdot}42 \times 10^{-8}$.

Allowing for the inaccuracy of the measurements and the complexity of the decomposition products of acetaldehyde, the results indicate that two molecules are chemically activated for each quantum absorbed.

Experiments with Acetone Vapour.

The same apparatus was used except that an air-bath was placed round the reaction bulb to keep the acetone as an unsaturated vapour at about 750 mm. and 60°. The amount of light absorbed was taken to be equal to that measured in the experiments on aqueous solutions of acetone described below, as, the concentrations of acetone being equal, it has been shown that the extinction coefficients of gaseous and of dissolved acetone are not very different (Porter and Iddings, *J. Amer. Chem. Soc.*, 1926, **48**, 40). The results were :

Vol. of bulb (c.c.).	Exposure (mins.).	Press. change (cm. Hg).	No. of g.-mols. acetone decomp. per sec.
125	245	2·42	$1{\cdot}34 \times 10^{-8}$
80	160	3·63	$1{\cdot}81 \times 10^{-8}$ (mean)
80	135	3·35	

Number of gram-molecular quanta absorbed per sec. $= 1{\cdot}0 \times 10^{-8}$.

Other experiments were made at room temperature in an apparatus consisting of two bulbs filled with acetone vapour connected by a U-tube containing liquid acetone. The apparatus was immersed in a thermostat before and after exposing one bulb (of quartz) to the lamp, and the photochemical change determined by the change in level of the liquid in the U-tube. The energy in the light absorbed was directly measured with the oxalic acid–uranyl sulphate solution. The results were :

Exposure = 1 hour. Volume of bulb = 125 c.c.

Pressure change (cm. Hg) = 0·212, 0·176, 0·141, 0·159, 0·247.

Taking the average as 0·187 cm. Hg, the number of g.-mol. of acetone decomposed per second is 2×10^{-9}. The mean of several oxalic acid titrations gave the number of gram-molecular quanta per second $= 4{\cdot}85 \times 10^{-9}$. The number of molecules chemically changed is very close to the number of quanta absorbed.

The accuracy of these low-pressure measurements was not so great as that of the high-pressure ones, so that it is not certain whether the diminution in quantum sensitivity is real or due to experimental errors.

A further series of experiments was made with hot acetone vapour, oxalic acid–uranyl sulphate solutions being used to measure the absorption.

The results were : Volume of bulb = 125 c.c. Exposure = 60 minutes. Pressure change (cm. Hg.) = 0·60, 0·82, 0·815, 0·77, 0·71, 0·80, 0·60, 0·90.

Taking the mean as 0·75, the number of g.-mol. of acetone decomposed per second = $1{\cdot}5 \times 10^{-8}$.

The mean of several oxalic acid titrations gave the number of gram-molecular quanta absorbed per second = $0{\cdot}867 \times 10^{-8}$.

It seems that about two molecules of acetone are decomposed for each quantum absorbed.

Experiments with Aqueous Solutions of Acetone.

It is stated by Henri (*Compt. rend.*, 1913, **156**, 1012) that about 1300 molecules of acetone are hydrolysed for each quantum of ultraviolet light absorbed. He appears to have used an open quartz cell to contain the solution, and must have lost acetone by evaporation. In our experiments, solutions of acetone were exposed in a closed plane-walled quartz cell to an approximately parallel beam of ultra-violet light, and the number of quanta absorbed measured with the oxalic acid–uranyl sulphate solution. When the acetone solution was titrated iodimetrically, the photochemical change was too small to be measurable, although if the reaction followed the Einstein–Stark law it should have been recognisable. The acetic acid formed was therefore estimated with very dilute baryta solution, and the following mean results were obtained :

Conc. of acetone solution %.	G.-mols. acetic acid formed per sec.	G.-molecular quanta absorbed per sec.
0·3	$5{\cdot}7 \times 10^{-10}$	$1{\cdot}0 \times 10^{-8}$
15	$2{\cdot}88 \times 10^{-9}$	$1{\cdot}9 \times 10^{-8}$

Here the number of g.-mols. of acetic acid formed is less than one-fifth of the number of quanta absorbed. It is possible that formation of other products occurs, but these could not be discovered or estimated, and the results must be taken to be in serious disagreement with those of Henri.

These measurements emphasise the need for reinvestigation of older results on the ratio of the number of molecules reacting to the number of quanta absorbed in photochemical reactions. Correcting the tables of such reactions examined from this point of view which were presented to the Faraday Society in October, 1925 (Allmand, Dhar, and Mukerji), we now find that in 65% of the cases the number of molecules reacting is, within a factor of about 3, equal to the number of molecules physically activated, indicating fairly simple mechanisms in all these examples. In 20% of the cases, chiefly those involving halogen molecules, the number of molecules changed is many times the number of quanta absorbed, indicating " chain " mechanisms. It is characteristic of this class of reaction that "inhibitors" produce their large effect by interfering with the "chains." In 15% of the cases, the number of molecules reacting is much less than the number of quanta absorbed, and in some of these cases, again involving the halogens, we find long lives of activated molecules (Briers, Chapman, and Walters, this vol., p. 562; Eggert, *Physikal. Z.*, 1925, **26**, 865), and reaction rates varying with the square root of the light absorbed (Bodenstein and Lütkemeyer, *Z. physikal. Chem.*, 1924, **114**, 208; Berthoud and Bellenot, *J. Chim. phys.*, 1924, **21**, 308), all indicating a primary dissociation of the halogen molecule, followed by extensive slow recombination of the atoms produced, only an occasional atom entering into the observed chemical change. There is need for much work to elucidate the complexities of these last two classes of reactions. It is significant, however, that the first class of reactions should be the largest; here apparently every molecule physically activated takes part in chemical change, showing that under these conditions, when a molecule is activated, its chemical reactivity on collision is not affected by its orientation.

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