process in dehydration and final purification of cyclic nitrogen compounds of basic type.

Summary

A simple economical method involving the use of zinc chloride is presented for the purification of basic nitrogenous substances. The process includes the removal in one operation of water hydrocarbons, thio and phenolic bodies and other associated non-basic admixtures. The process permits the recovery and re-use of the zinc chloride.

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[CONTRIBUTION FROM THE DANIEL SIEFF RESEARCH INSTITUTE]

The Photochemical Decomposition of Aliphatic Alcohols in Aqueous Solution

BY L. FARKAS AND Y. HIRSHBERG

The absorption spectra and the photochemical decomposition of methyl and ethyl alcohols in the gaseous state have been investigated recently. The absorption spectra consist of continuous bands, extending from 2000 Å. to the far ultraviolet.[1] The photochemical decomposition is consequently a dissociation process, which takes place according to the scheme[2,3]

$$\text{ROH} + h\nu \longrightarrow \text{aldehyde} + \text{H}_2 \qquad (1)$$

According to Patat this is the primary process, since no hydrogen atoms (formed for example according to RO + H) could be detected by the parahydrogen method.

It seemed interesting to investigate the photochemical decomposition of the aliphatic alcohols also in solution in order to determine the primary process and to obtain some information about the interaction of photochemically formed products with the water.

Experimental

A water-cooled vertically burning mercury lamp was used as light source, surrounded concentrically by two reaction vessels, as used already in previous investigations.[4,5] The light intensity was usually checked by determining the decomposition of monochloroacetic acid. Although the decomposition of monochloroacetic acid takes place also in the region 2600–2000 Å., in which the alcoholic solutions do not absorb light, it was found that the intensity of the mercury arc in the short wave length region (below 2000 Å.) was proportinal to the intensity of light which is active in the hydrolysis of monochloroacetic acid. Two mercury arcs of different sizes were used. The one had a quantum output of 1.5 × 10^{19} per second, the other about 3–5 × 10^{18} per second. The number of alcohol molecules decomposed per second was about 20–40 times smaller.

The alcoholic solutions were made from purest alcohol and distilled water, their concentration was usually 1 to 3 molar. Aqueous solutions of methyl alcohol, ethyl alcohol, propyl alcohol and isopropyl alcohol were investigated, the first two of these solutions more in detail.

Experiments with Methyl and Ethyl Alcohols

After the aqueous solutions of these two alcohols were illuminated with the full light of the mercury arc for some time, gas was evolved, which proved to be pure hydrogen without any carbon monoxide or dioxide content. This suggests that the decomposition of methyl and ethyl alcohol also in solution takes place according to

$$\text{CH}_3\text{OH} + h\nu \longrightarrow \text{H}_2\text{CO} + \text{H}_2$$
$$\text{CH}_3\text{CH}_2\text{OH} + h\nu \longrightarrow \text{CH}_3\text{CHO} + \text{H}_2$$

In fact in all cases formation of aldehyde could be proved qualitatively. For the quantitative determination different methods were used: formaldehyde was determined either according to Romijn by oxidation with alkaline iodine solution or by oxidation with hydrogen peroxide to formic acid and titrating the acid with sodium hydroxide; or according to Ripper[6] with bisulfite and iodine. The latter method and the reaction with hydroxylamine sulfate was used for the estimation of acetaldehyde. The results obtained by the different methods were in satisfactory agreement.

Tables I and II contain the results of some experiments on the decomposition of methyl and ethyl alcohols.

TABLE I

EXPERIMENTS WITH 2 MOLAR AQUEOUS SOLUTIONS OF METHYL ALCOHOL

Minutes, illuminated	Moles H_2, evolved	Moles, aldehyde found	Intensity: number of $ClCH_2COOH$, decomposed
210	4.0 × 10^{-3}	2.1 × 10^{-3}	2.6 × 10^{18} sec.$^{-1}$
140	2.8 × 10^{-3}	1.1 × 10^{-3}	..
280	6.4 × 10^{-3}	2.7 × 10^{-3}	..
150	3.9 × 10^{-3}	2.5 × 10^{-3}	3.6 × 10^{18} sec.$^{-1}$
240	5.7 × 10^{-3}	3.0 × 10^{-3}	4.0 × 10^{18} sec.$^{-1}$
15	..	0.4 × 10^{-3}	3.1 × 10^{18} sec.$^{-1}$

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[1] G. Herzberg and G. Scheibe, *Z. physik. Chem.*, **B7**, 390 (1930).

[2] See Farkas's communication to K. E. Bonhoeffer, *Z. Elektrochem.*, **40**, 425 (1934).

[3] E. Patat, *ibid.*, **41**, 494 (1935).

[4] L. Farkas and O. J. Wansbrough-Jones, *Z. physik. Chem.*, **B18**, 124 (1932).

[5] L. Farkas, *ibid.*, **B23**, 89 (1933).

[6] *Cf.* G. Wagner, *Biochem. Z.*, **194**, 441 (1928).

TABLE II

EXPERIMENTS WITH 2 MOLAR AQUEOUS SOLUTIONS OF ETHYL ALCOHOL

Minutes, illuminated	Moles, H_2 evolved	Moles, aldehyde found	Intensity . number of $ClCH_2COOH$, decomposed
210	2.3×10^{-3}	..	2.1×10^{18} sec.$^{-1}$
120	2.6×10^{-3}	0.2×10^{-3}	..
120	1.9×10^{-3}	0.2×10^{-3}	..
135	7.0×10^{-3}	..	11.0×10^{18} sec.$^{-1}$
80	2.6×10^{-3}	0.15×10^{-3}	..

It will be seen from the two tables that the aldehyde found in the illuminated solution was always less than the amount of hydrogen formed in the photochemical decomposition. About 50% of the theoretical yield of formaldehyde is found, in the case of acetaldehyde even less than 10%. This can be due to two reasons: (a) the photochemical decomposition of alcohols gives hydrogen also by other reaction than (1); (b) the photochemically formed aldehyde is decomposed subsequently during the illumination. With regard to the first possibility the formation of acids from alcohols according to

$$RCH_2OH \xrightarrow{h\nu} R'C{=}CO + 2H_2 \xrightarrow{+H_2O} RCOOH$$

may be probable. It was, however, not possible to detect any formation of acid (which of course should be present in form of an ester) in either of the illuminated solutions of methyl and ethyl alcohols.

On the other hand, as it is shown in a subsequent paper,[7] acetaldehyde solutions are decomposed readily in ultraviolet light and give only liquid reaction products. Since acetaldehyde absorbs ultraviolet light in the region 2900–2000 Å., where the ethyl alcohol solution does not absorb light, it is clear that the photochemically formed acetaldehyde will be decomposed also during the illumination and only one part of it will be found afterward. This was tested directly also by adding small amounts of acetaldehyde to the ethyl alcohol solution and illuminating the mixture. For instance 100 cc. of a 5 molar solution of ethyl alcohol with 1.8×10^{-3} moles of acetaldehyde contained only 0.4×10^{-3} mole of aldehyde after forty-five minutes of illumination. Since in this time 2×10^{-3} mole of hydrogen was evolved, altogether 3.4×10^{-3} mole of acetaldehyde was decomposed. This corresponds to the rate of decomposition of acetaldehyde solutions under the influence of the mercury are employed.[8] In the case of the methyl alcohol a much smaller part of the aldehyde formed photochemically is decomposed subsequently. This is also in agreement with experiments on the photochemical decomposition of aqueous formaldehyde solutions.[7]

Since aqueous formaldehyde absorbs ultraviolet light only below 2350 Å.,[9] it is exposed to the action of the much less intense light than acetaldehyde which is sensitive to all the light below 2900 Å. This is the reason why comparatively more aldehyde is found in the photolysis of methyl alcohol than in that of ethyl alcohol.

Concerning the mechanism of the decomposition in the gaseous state F. Patat[3] suggested that the formation of hydrogen and aldehyde takes place in one step rather than through intermediate radicals such as $RCH_2 + H$ which might give $RCHO + H_2$ in a bimolecular reaction. It is difficult to discriminate between different possible mechanisms in solution, since in solution there is also a possibility of the participation of water in the formation of the final products of the decomposition. In the case of the photochemical decomposition of the aliphatic acids, in water solution it was found that there are two possibilities for the formation of the final products, according to the reactions

$$RCOOH + h\nu \longrightarrow \boxed{\begin{array}{c}H\\R\end{array}} + \boxed{\begin{array}{l}OH\\COOH\end{array}} \longrightarrow RH + CO_2 \qquad (2)$$

$$RCOOH + h\nu \longrightarrow \boxed{\begin{array}{r}HO\\R\end{array}} + \boxed{\begin{array}{l}H\\COOH\end{array}} \longrightarrow ROH + HCOOH \qquad (3)$$

Apparently the water molecule reacts in two different ways with the primary products of the photochemical reaction, which is either an excited acid molecule or its dissociation products such as R + COOH. In solution it may happen that the molecule which has absorbed light reacts with the solvent even before the actual dissociation[4,5,10] of the molecule takes place.

This is possible since there is nearly a continuous interaction between the molecule and the solvent and the energy of the absorbed light may be utilized to bring about reactions with or without the participation of the solvent. Furthermore, the quantum yield of photochemical reactions occurring in a continuous absorption region is in liquids often smaller than unity, since deactivation during the absorption process may take place by collisions with the solvent.

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[7] Y. Hirshberg and L. Farkas, THIS JOURNAL, **59**, 2453 (1937).

[8] The intensity of the mercury arc measured with the hydrolysis of monochloroacetic acid, was 1.2×10^{19} chlor ions per second.

[9] V. Henri and A. Schou, *Z. Physik*, **49**, 114 (1928).

[10] J. Franck and E. Rabinowitsch, *Trans. Faraday Soc.*, **30**, 120 (1934).

TABLE III

Time of illumination forty-five minutes

	In reaction vessel I	II	Cl-ions formed	H_2 evolved	Quantum yield
(a)	H_2O	$ClCH_2COOH$	12.3×10^{18} sec.$^{-1}$	....	0.8
(b)	5m. C_2H_5OH	$ClCH_2COOH$	11.8×10^{18} sec.$^{-1}$	3.5×10^{17} sec.$^{-1}$	

In the case of the decomposition of methyl and ethyl alcohol solutions it is also possible that the excited alcohol molecule or its primary dissociation products react with water. In the case of ethyl alcohol the photochemical reaction with the participation of water may be written as

$$CH_3CH_2OH + h\nu \longrightarrow \begin{array}{r} HO \\ CH_3CH_2O \end{array} + \begin{array}{c} H \\ H \end{array} \qquad (4)$$

The other possible reaction in analogy to (3) is a reverse reaction. The final products of the decomposition are again H_2 + aldehyde just as in the gaseous state. With regard to the formation of H_2 one can state that one of its H-atoms is coming from the OH group or from the water, the other certainly from one of the H atoms bound directly to carbon. This can be shown directly by investigating the isotopic composition of hydrogen samples which were formed by the photochemical decomposition of ordinary alcohol in pure heavy water. The analysis was made by the micro-heat conductivity method.[11] The hydrogen thus evolved had 50% D content in agreement with the suggested mechanism.

In order to estimate the extent of the deactivation, the quantum yield of the photochemical decomposition of ethyl alcohol was determined.

The method used for the determination of the quantum yield was the same as in a previous communication[4]; the decomposition of monochloroacetic acid was determined: (a) when the light of the mercury arc passed through water, (b) when the light passed through 5 molar alcohol solution. Since in case (a) all the light which acts in the decomposition of the alcohol solution was absorbed by the monochloroacetic acid, the quantum yield of the alcohol decomposition is $c/(a - b)$ 0.9 if a and b are the number of monochloroacetic acid molecules decomposed in cases (a) and (b), respectively, and c the number of alcohol molecules decomposed. The factor 0.9 is the quantum yield of the photolysis of monochloroacetic acid in the region 2000 Å.[4] Table III contains the data of such an experiment.

It will be seen that the quantum yield of the ethyl alcohol decomposition is nearly unity; the deactivation by the solvent and the extent of reverse reaction evidently is small.

The photochemical decomposition of propyl alcohol is analogous to that of ethyl alcohol. The decomposition takes place according to

$$CH_3CH_2CH_2OH + h\nu \longrightarrow CH_3CH_2CHO + H_2 \qquad (5)$$

The evolved gas was pure hydrogen; the formation of aldehyde could be demonstrated qualitatively. Again the amount of aldehyde is less than the amount of hydrogen evolved, evidently because the aldehyde is decomposed further.[7] For instance in an experiment when 4×10^{-3} mole of hydrogen was formed, only 1.1×10^{-3} mole of propionaldehyde was found by quantitative estimation.

The decomposition of isopropyl alcohol was interesting because one would expect in this case the formation of hydrogen and acetone.

In fact the experiments showed that this solution also evolved hydrogen on illumination, but no acetone could be found qualitatively. Nevertheless the formation of acetone is made probable by the fact that the evolved gas contained beside hydrogen 20–25% of methane, which is one of the decomposition products of acetone in ultraviolet light. The acetone[12] primarily formed from isopropyl alcohol is further decomposed according to

$$CH_3COCH_3 + h\nu \xrightarrow{+H_2O} CH_4 + CH_3COOH \qquad (6)$$

It was shown by blank experiments that under our conditions small amounts of acetone added to the isopropyl alcohol solution were decomposed to such an extent that its presence could not be detected after some time of illumination.

Summary

1. The photochemical decomposition of methyl alcohol, ethyl alcohol, and propyl alcohol in aqueous solution takes place according to

$$ROH + h\nu = H_2 + \text{aldehyde} \qquad (1)$$

No other gas than hydrogen is formed. The aldehyde is decomposed partly in a subsequent photochemical reaction.

2. By investigating the isotopic composition of the hydrogen evolved from alcohol dissolved in heavy water it could be shown that one of the H atoms of hydrogen is coming off the OH group.

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(11) A. Farkas and L. Farkas, *Proc. Roy. Soc.* (London), **A144**, 467 (1934).

(12) Ciamician and Silber, *Ber.* **36**, 1582 (1903).

the other from the hydrogen bound directly to carbon.

3. The quantum yield of the decomposition of ethyl alcohol is 0.8.

4. Isopropyl alcohol is decomposed according to

$$\mathrm{CH_3CH(OH)CH_3} \longrightarrow \mathrm{CH_3COCH_3} + \mathrm{H_2} \qquad (2)$$

the acetone being decomposed in a subsequent reaction.

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On the Photochemical Decomposition of Aliphatic Aldehydes in Aqueous Solutions

BY Y. HIRSHBERG AND L. FARKAS

The photochemical decomposition of the aliphatic aldehydes in the gaseous state has been investigated thoroughly in the last few years.[1-5] It was found that under the influence of ultraviolet light absorbed below 3000 Å. the aldehydes are decomposed mainly according to

$$\mathrm{RCHO} + h\nu \longrightarrow \mathrm{RH} + \mathrm{CO} \qquad (1)$$

yielding hydrocarbon and carbon monoxide (in the case of formaldehyde CO + H_2) as main products. Only a few per cent. of hydrogen and RR hydrocarbon is formed. The reactions

$$\mathrm{RCHO} + h\nu \begin{array}{ll} \nearrow \mathrm{RH} + \mathrm{CO} & \text{(1a)} \\ \searrow \mathrm{R} + \mathrm{H} + \mathrm{CO} & \text{(1b)} \end{array}$$

were suggested as primary processes, (1a) being the more probable one. Reaction (1b) gives RH, H_2 and R–R in secondary reactions and is practically equivalent to another possible primary reaction

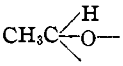
$$\mathrm{RCHO} + h\nu \longrightarrow \mathrm{R} + \mathrm{HCO} \qquad (1c)$$

which gives in secondary reactions also RH + H_2 + RR; RH is the main product if the primary process is followed preferentially by the bimolecular reaction

$$\mathrm{R} + \mathrm{HCO} \longrightarrow \mathrm{RH} + \mathrm{CO}$$

Beside these reactions a polymerization was observed to some extent.[4-6] The formation of radicals as expressed in (1b) and (1c) by light absorption of the aldehydes follows from the experiments of Leermakers,[7] Akeroyd and Norrish[8] and Patat,[9,10] from the investigation of the thermal and photochemical autoxidation of the aldehydes. Leermakers and Akeroyd and Norrish found that above 80° the photolysis of acetaldehyde is a chain reaction and some radicals which are formed by the photochemical primary process initiate the chains. The formation of H atoms in the continuous absorption spectrum of formaldehyde was shown directly by Patat: the H atoms formed by the photochemical decomposition induce a para–ortho conversion of hydrogen which is added to the formaldehyde.

The thermal oxidation of acetaldehyde is also a chain reaction, in which, according to Bodenstein,[11] aldehyde molecules with unsaturated valences such as



$$\mathrm{CH_3C}\begin{array}{l} \diagup \mathrm{H} \\ -\mathrm{O}- \\ \diagdown \end{array}$$

initiate and carry the chain. Bowen and Tietz[12] and recently Carruthers and Norrish[13] investigated the photochemical oxidation of formaldehyde and acetaldehyde and found that light absorption in the presence of oxygen leads to chains similar to those of the thermal oxidation with an approximate chain length of 20. In the case of acetaldehyde the same sort of reaction occurs in gaseous state, in the pure liquid and in solutions of water, hexane and acetic acid. These experiments show not only that the light absorption of aldehydes must give a reactive compound or reactive radicals, but also indicate that in liquid and in solution intermediate products with long life-time are involved. In the case of benzaldehyde Baeckstroem[14,15] showed that the primary product of the

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[1] F. W. Kirkbridge and R. W. C. Norrish, *Trans. Faraday Soc.*, **27**, 404 (1931).

[2] F. W. Kirkbridge and R. W. C. Norrish, *ibid.*, **29**, 103 (1933).

[3] F. W. Kirkbridge and R. W. C. Norrish, *J. Chem. Soc.*, 1518 (1932).

[4] P. A. Leighton and F. E. Blacet, THIS JOURNAL, **54**, 3165 (1932).

[5] P. A. Leighton and F. E. Blacet, *ibid.*, **55**, 1766 (1933).

[6] J. E. Carruthers and R. G. W. Norrish, *Trans. Faraday Soc.*, **32**, 195 (1936).

[7] J. A. Leermakers, THIS JOURNAL, **56**, 1537 (1934).

[8] E. I. Akeroyd and R. G. W. Norrish, *J. Chem. Soc.*, 890 (1936).

[9] F. Patat, *Z. physik. Chem.*, **B25**, 208 (1934).

[10] F. Patat and T. Locker, *ibid.*, **B27**, 431 (1934).

[11] Bodenstein, *Berliner Ber.*, **111**, 18 (1931).

[12] E. J. Bowen and E. L. Tietz, *J. Chem. Soc.*, 234 (1930).

[13] J. E. Carruthers and R. G. W. Norrish, *ibid.*, 1036 (1936).

[14] Baeckstroem, *Z. physik. Chem.*, **B25**, 99 (1934).

[15] *Cf.* Bonhoeffer, *Z. Elektrochem.*, **40**, 425 (1934).