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Summary

The inhibition of the proteolytic action of trypsin by soaps has been studied using crystalline trypsin and pure soaps. The effect appears to be reversible. A simple system for the quantitative study of the phenomenon has been described. The inhibition of tryptic action by soaps may be an example of a general soap-protein reaction.

The Photolysis of Methyl Acetate

BY WALTER L. ROTH AND G. K. ROLLEFSON

In a recent paper Royal and Rollefson[1] reported observations on the photolysis of methyl formate. They showed, by means of experiments with metallic mirrors, that free radicals are formed in the decomposition of that compound and also in the photolysis of methyl acetate. In this paper we wish to present the results of analyses of the decomposition products of the latter compound and to interpret these results in terms of a reaction mechanism. In our experiments the energy necessary to bring about the reaction was introduced into the methyl acetate molecule in two ways. These were (1) by the absorption of light by the acetate molecule, and (2) by the absorption of the 2537 Å. line by mercury vapor in the reaction vessel followed by the reaction of this activated atom with the acetate molecules. Measurements of the absorption of light by the system showed that in the absence of mercury vapor there was no appreciable absorption at 2537 Å. Hence the two modes of activation can be studied separately.

Experimental

Apparatus and Materials.—The apparatus was essentially the same as that of Royal and Rollefson. Two types of light sources were used: (1) a quartz capillary mercury arc of the kind described by Atwood and Rollefson,[2] and (2) a low pressure gas filled resonance arc[3] which was operated at 25 milliamperes and 15.000 volts. The second arc was used for the mercury sensitized reaction in which the effective wave length was the 2537 line. In the capillary arc the resonance radiation was reversed and the other radiation near 2537 Å. was not absorbed so the effective energy was that supplied by the lines in the mercury spectrum between 2537 and the transmission limit of quartz. Since no filters were used all of these lines were involved but the principal one is that at 1942 Å.

The methyl acetate was from the same lot as had been used for the mirror experiments. The nitric oxide was obtained from Dr. Atwood, who had prepared it by the method of Johnston and Giauque.[4]

Procedure.—The reaction vessel and connecting tubing were evacuated to a pressure of 10^{-5} mm. or less, methyl acetate introduced to the desired pressure, and the temperature noted. The system was illuminated until a suitable amount of reaction had occurred as shown by the pressure change. The products were separated into three fractions as follows.

—185° Fraction.—The cell was immersed in liquid air and those gases not condensed were pumped into the gas buret. The residual products were warmed to room temperature and the pressure noted. In all cases, the moles of gas measured in the buret agreed satisfactorily with the value calculated from pressure differences. The fraction then was forced into a small gas holder and subsequently analyzed.

—117° Fraction.—This fraction represents those gases not condensable at the melting point of ethyl alcohol. The residual reaction mixture was distilled into a small (1-cc. capacity) tube equipped with a stopcock. A Dewar flask containing a solid–liquid ethyl alcohol mixture was placed around the tube, and after temperature equilibrium was established the stopcock was opened and the non-condensed gases expanded into the 500-cc. volume of the Toepler pump. Then the stopcock was closed, the gases in the pump forced into the gas buret, and the process repeated. (The quantity of gases measured in the buret was usually found to be somewhat less than that calculated from the pressure data. The buret values were far more consistent and were used for subsequent calculations.)

Residual Fraction.—This fraction represents those products which are condensable at room temperature and atmospheric pressure. After their pressure as gases was measured in the reaction vessel, they were distilled into a 50 cc. flask which contained 10 cc. of water. The flask was attached to the vacuum line through two ground joints and a stopcock, arranged so the flask could be detached and opened for analysis.

Analytical Methods.—Gas analyses were made in a microburet of the type described by Blacet and Leighton, and

(1) Royal and Rollefson, THIS JOURNAL, **63**, 1521 (1941).

(2) Atwood and Rollefson, J. Chem. Phys., **9**, 506 (1941).

(3) Noyes and Leighton, "The Photochemistry of Gases," Reinhold Publishing Corp., New York, N. Y., 1941, p. 38.

(4) Johnston and Giauque, THIS JOURNAL, **51**, 3194 (1929).

others.[5] Unless precluded by the size of sample, duplicate analyses were made.

Methyl acetate was determined by hydrolyzing with base. A 5-cc. aliquot of the aqueous solution containing the ester was pipetted into a 30-cc. Pyrex glass bomb tube and 1 cc. of 0.1 N sodium hydroxide added. The tube was sealed, heated at 100° for one hour, cooled, and titrated with 0.0100 N hydrochloric acid to the phenolphthalein end-point. Two blanks containing 5 cc. of water and 1 cc. of sodium hydroxide were treated in an identical manner, and the difference in titers taken as equivalent to the methyl acetate.

Diacetyl was analyzed colorimetrically.[6] The procedure entails converting the diacetyl to dimethylglyoxime, and comparing the red color developed in the presence of ferrous sulfate with that developed in dimethylglyoxime standards. Acetone, methyl acetate, and methyl alcohol were shown not to interfere.

Acetone was analyzed colorimetrically.[7] When a solution of the ketone, salicylaldehyde, and potassium hydroxide is heated, an orange color is developed which may be compared with colors developed in acetone standards. Methyl acetate, diacetyl, and methyl alcohol were shown not to interfere.

Methyl alcohol was determined by oxidizing to formaldehyde with an acid solution of potassium permanganate.[8] The excess permanganate was destroyed with oxalic acid and the color developed with Schiff reagent compared with that developed in standard methanol solutions. Methyl acetate, diacetyl and acetone did not interfere.

Experimental Results

Experiments with the capillary mercury arc were carried out both with and without mercury vapor in the reaction vessel. It was found that the rate of the reaction was the same under both sets of conditions. On the other hand, with the low pressure resonance arc the rate with mercury vapor present was much faster than in its absence. One pair of experiments differed by a factor of eight. On the basis of such tests we concluded that we were dealing with the sensitized reaction when we used the resonance arc and with the unsensitized reaction when the other arc was used.

Analysis of the reaction products showed that the same substances were produced under both sets of conditions but the proportions were somewhat different. The substances found were: carbon monoxide, carbon dioxide, hydrogen, methane, ethane, acetone, diacetyl, and methyl alcohol. Qualitative tests for aldehydes, dimethyl ether, unsaturated hydrocarbons, and

peroxides showed none present. The composition of the mixture of products varied with the degree of completion of the reaction but not with the light intensity. Complete decomposition of the ester resulted in a pressure increase between one and two times the initial pressure of the ester. It was found convenient to use this pressure increase as a rough measure of the extent to which the reaction had proceeded in any given experiment. In the tables of data this is represented by $\Delta n/n_0$, i. e., the change in the number of moles of gaseous substances present divided by the number originally present.

It was not found possible to analyze for the small amounts of methanol usually obtained in the decomposition runs so the values listed for that substance in the tables were obtained by difference. For that purpose it was assumed that the most condensable fraction of the reaction mixture consisted of methanol, acetone, diacetyl, and methyl acetate but no other substances. As a check on the validity of this assumption a large amount of this residue was collected by carrying out the reaction in a three-liter bulb fitted with a quartz window. The results obtained showed that the material was 66.2% methyl acetate, 5.4% diacetyl, 5.0% acetone, and 23.0% methanol, thus accounting for 99.6% of the substance collected.

Tests of the analytical method used for the methyl acetate showed that it was capable of an accuracy of one per cent., but it was found that the results obtained in analyzing the reaction mixtures did not agree as well as they should on the basis of this test. Since the methanol was determined by difference, such variations were undesirable; therefore, instead of analyzing each set of reaction products for unchanged ester an empirical curve was obtained for the amount of acetate decomposed as a function of the observed $\Delta n/n_0$. The amount of ester remaining in any given experiment was read from this curve. The data for the curve are shown in Table I.

(5) (a) Blacet and Leighton, *Ind. Eng. Chem., Anal. Ed.,* **3**, 766 (1931); (b) Blacet, MacDonald, and Leighton, *ibid.,* **5**, 272 (1933); (c) Blacet and MacDonald, *ibid.,* **6**, 334 (1934); (d) Blacet and Volman, *ibid.,* **9**, 44 (1937).

(6) Prill and Hammer, *Iowa State Col. J. Sci.,* **12**, 385 (1938).

(7) Korenman, *J. Applied Chem.* (U. S. S. R.), **6**, 1002 (1933).

(8) Snell, "Colorimetric Methods of Analysis," D. Van Nostrand Co., Inc., New York, N. Y., 1937.

TABLE I

METHYL ACETATE ANALYSES AT VARIOUS VALUES OF $\Delta n/n_0$

m_i = initial moles $CH_3CO_2CH_3$; m_f = final moles $CH_3CO_2CH_3$.

$\Delta n/n_0$	m_i	m_f	$\Delta n/n_0$	m_i	m_f
0	9.77	9.77	0.673	9.77	3.90
0.086	9.65	7.80	.685	9.73	3.72
.197	9.82	7.64	.971	9.69	3.26
.275	9.68	6.36	1.41	9.78	1.80
.517	9.68	5.30			

TABLE II

PRODUCTS OF THE MERCURY SENSITIZED DECOMPOSITION OF METHYL ACETATE

Initial amount of ester, 9.7 $\pm$ 0.15 $\times$ 10^{-5} mole in 114 cc.

% CH₃CO₂CH₃ decomposed	Products (moles per 100 moles ester decomposed)								Material balance		
	H₂	CO	CH₄	CO₂	C₂H₆	(CH₃CO)₂	(CH₃)₂CO	CH₃OH	C	H	O
13.6	1.8	37.4	6.9	3.0	6.0	21.0	23.9	73.2	3.00	6.54	1.90
20.2	2.8	44.5	7.9	3.6	10.6	18.8	20.3	62.5	3.00	6.35	1.92
26.1	3.3	35.2	7.4	3.1	5.8	15.0	21.4	84.5	3.00	6.55	1.85
32.0	4.6	51.0	9.5	6.4	10.8	12.5	25.0	61.9	3.00	6.16	1.85
49.9	4.2	76.0	13.7	7.5	15.1	8.1	18.0	61.1	3.00	6.05	2.03
52.3	10.6	72.3	16.4	6.0	14.4	6.5	15.7	58.0	3.00	6.32	2.01
58.3	11.1	81.3	18.1	8.9	21.6	5.0	15.6	53.7	3.00	6.21	1.97
69.2	22.8	98.8	25.3	10.0	27.1	1.5	12.2	51.5	3.00	6.36	1.97
69.2	19.6	96.8	24.7	9.9	29.8	2.0	8.4	45.3	3.00	6.26	1.94
82.1	29.2	108.2	39.8	13.1	32.5	0	7.0	32.6	3.00	5.88	1.76
86.0	31.4	119.8	49.5	16.8	34.0	0	4.0	25.1	3.00	6.06	1.88
93.7	21.5	132.0	94.1	23.0	32.4	0	0	20.3	3.00	6.25	1.78
94.8	29.7	120.6	89.9	23.7	18.3	0	0	25.5	3.00	6.40	1.96

TABLE III

COMPARISON OF PRODUCTS OF SENSITIZED AND NON-SENSITIZED PHOTOLYSIS OF METHYL ACETATE

Reaction cell, 114 cc.; temperature, 20°: sensitized reaction indicated by S, non-sensitized by R.

	Initial CH₃CO₂CH₃ moles × 10⁵	Δn/n₀	H₂	CO	CH₄	Products (mole %) CO₂	C₂H₆	(CH₃CO)₂	(CH₃)₂CO	CH₃OH
S	9.84	0.086	0.9	15.7	4.2	2.3	4.6	12.1	13.9	46.3
R	9.58	.104	1.4	20.6	6.9	9.8	10.8	6.9	15.6	28.0
S	9.77	.143	1.8	25.6	4.6	2.0	6.2	10.8	13.1	35.9
R	10.28	.205	1.9	34.5	11.4	11.7	14.6	2.2	9.4	14.3
S	9.78	1.41	10.7	43.3	14.6	4.8	12.0	0	2.6	12.0
R	9.93	1.08	3.5	37.3	8.1	14.6	20.1	0	3.8	12.6

The complete analytical results for a series of measurements of the mercury sensitized decomposition are shown in Table II. The last three columns in the table show the correspondence of the analyses to the empirical formula of the ester. It is apparent that the total hydrogen runs slightly high and the total oxygen low if the carbon is as-

Fig. 1.—Products per 100 moles of methyl acetate decomposed.

sumed to be correct. The composition of the products is expressed as moles of each product formed for every 100 moles of ester decomposed. The variation is shown graphically in Fig. 1.

The Unsensitized Photolysis.—The decomposition by direct absorption of light by the methyl acetate molecule was obtained by using the high pressure arc which does not give any appreciable amount of the resonance radiation. A comparison of the composition of the decomposition products under closely similar conditions is shown in Table III. The same products are found but the distribution is different.

Effect of Light Intensity.—The intensity of the light causing the decomposition was varied by increasing the distance of the arc from the cell from 3 to 83 mm. No significant change in the composition of the products was observed.

Effect of Nitric Oxide on the Reaction.—Several experiments were performed with nitric oxide present in the reaction mixture. The results are not as clean cut as in many other experiments of this kind since the nitric oxide undergoes decomposition on illumination with the wave lengths which bring about the decomposition of the acetate. It is of interest, however,
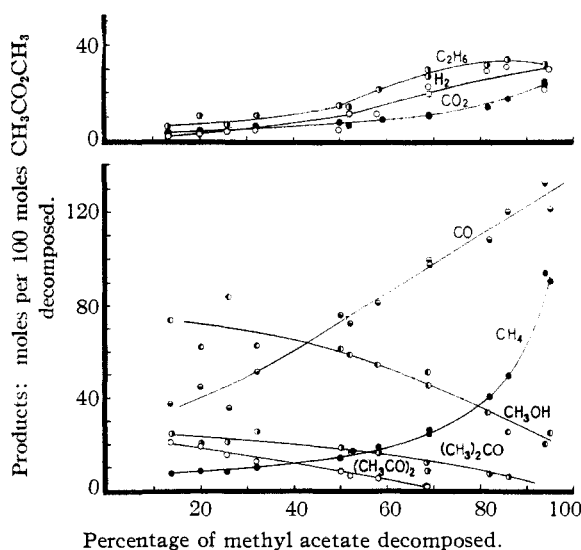
that the presence of this oxide eliminated the formation of methane, ethane and hydrogen.

Discussion.—The difference in the composition of the products of the sensitized and unsensitized reactions is to be attributed, at least partially, to the difference in the light sources. The quartz capillary arc used in the unsensitized experiments emits a large amount of energy at wave lengths longer than 2500 Å., which is absorbed by such products as diacetyl and acetone. The decomposition of these substances increases the yield of the simple molecules. On the other hand, the resonance arc emits very little of the longer wave length radiation and therefore permits diacetyl and acetone to accumulate in the system. The results of the analyses are in accord with this picture. It is possible, however, that the difference is partially due to a difference in the stability of the radicals produced in the one case by the absorption of short wave length radiation and in the other by reaction with activated mercury atoms.

The large amounts of diacetyl and acetone found in the products suggest that one of the most important primary processes is the rupture of the methyl acetate molecule into an acetyl and a methoxy radical. From the analysis of the products in the experiment in which only 13.6% of the ester was decomposed, we find the number of acetyl radicals recovered in the form of diacetyl and acetone is two-thirds the number of ester molecules decomposed. Since both of these molecules are decomposed in secondary reactions, this figure is a minimum and we can conclude from this observation alone that at least two-thirds of the ester molecules break in such a way as to yield an acetyl radical. Actually, if we write equations so as to account for the conversion of the remaining fragments of the molecules into the ultimate products, we find that two molecules of the ester must react for each molecule of diacetyl or acetone formed. Viewing the analytical results in this way it is apparent that ninety-five per cent. of the ester molecules must break into acetyl and methoxy radicals.

It is impossible to decide definitely on the basis of experiments, such as have been described in this paper, exactly how the other products are formed. Methyl alcohol can be formed by a methoxy radical acquiring a hydrogen atom from some other molecule or radical. The small amount of carbon dioxide found could come from a rear-

rangement of the ester into ethane and carbon dioxide, but the absence of hydrocarbons in the products when nitric oxide was present suggests that a free radical mechanism is to be preferred for that process.

The facts pointed out in the preceding paragraphs lead to the conclusion that the decomposition of methyl acetate proceeds through a free radical mechanism exclusively. This is in marked contrast to the conclusions of Royal and Rollefson[1] in the case of methyl formate where nearly three-fourths of the reaction was believed to go through a rearrangement mechanism. This difference in interpretation is supported by the fact that although the rates of decomposition of the esters are practically the same when illuminated by the same light intensity at the same pressure, the number of radicals produced is much greater in the case of the acetate. The data presented by Royal and Rollefson on the rates of removal of metallic mirrors by illuminated streams of the vapors of the esters show that under the same conditions the acetate yields about three times as many radicals as the formate. According to their interpretation of their results approximately three-fourths of the formate decomposed by rearrangement mechanisms and the remainder by way of radicals. If this interpretation is accepted, then at least three-fourths of the acetate must decompose by the radical mechanisms. Since it is always possible that some of the products of any radical mechanism may be the same as those of rearrangement processes, these comparisons cannot be made too quantitative. It can be said, however, that a comparison of the decompositions of these two esters shows that the acetate decomposes primarily by a radical mechanism but the formate must involve considerable non-radical type reactions. Furthermore the mode of decomposition of the acetate is the same whether the energy is supplied by an activated mercury atom or by direct absorption of light by the ester.

Summary

The mercury sensitized and the non-sensitized photolyses of methyl acetate have been studied. The products of the reaction were found to be diacetyl, acetone, methyl alcohol, carbon monoxide, carbon dioxide, methane, ethane, and hydrogen. From a consideration of the relative proportions of the products, it has been concluded that the principal primary process is a splitting of the

ester molecule into an acetyl and a methoxy radical. The observed products are formed in

secondary reactions of these radicals.

Reproducible Contact Angles on Reproducible Metal Surfaces. I. Contact Angles of Water against Silver and Gold[1]

BY F. E. BARTELL AND PAUL H. CARDWELL

Data in the literature show that contact angles formed with water drops on paraffin and on other soft hydrophobic solids have been readily reproducible on different samples of the same solid, while contact angles formed with water on relatively hard solids have not been readily reproducible when different samples of the same solid were used. Apparently the surfaces of different samples of a given hard solid did not have identical properties even though the investigator may have used reasonable care in the preparation of these surfaces.

The surface tensions (and the corresponding free surface energies) of soft solids are low and adsorption effects must be low likewise. In contrast, the surface tensions of hard solids are relatively high, adsorption readily occurs and the clean surface of a pure solid may quickly become highly contaminated and thus altered in properties. It seems probable, then, that the failure of previous investigators to obtain reproducible contact angles upon surfaces of given hard solids has been due not so much to defects in methods of measurements as to the fact that the original surfaces of the solid material had become contaminated to different degrees.

Numerous investigators have observed that for a given system the angle of contact was not definite, but that it varied between limits. In some cases the difference between these limits was small, in other cases it was as great as 60° to 90°. The contact angle formed when a liquid was caused to advance over a solid was usually greater than the angle formed when the liquid was caused to recede. This difference in angles has been re-

ferred to as "hysteresis" of contact angles.[1a-6] Although various explanations have been offered to account for the existence of two different and fairly definite angles for a single three-phase system, no generally accepted explanation has been offered.

The principal objective of the present research was to determine the factors which have been responsible for the difficulties which have been experienced by those who have attempted to obtain reproducible and significant measurements of contact angles. This necessitated the preparation of solid surfaces with reproducible properties, and the development of a procedure for the formation and measurement of contact angles of a system which could be maintained under exact control.

Method of Preparing Solid Surfaces with Reproducible Properties.—In the preparation of the solid surfaces it was deemed desirable to know not only the final treatment history of the solid but also the complete history of the substance as a solid. To accomplish this the solid was formed in vacuum from the vapor phase. The relatively inert metals silver and gold seemed most suitable for study. Films of these metals were formed on Pyrex glass tips by vaporizing the metals in a vacuum of 10^{-5} mm. Vaporization of the metal was accomplished by suspending small bent pieces of the pure metal over a tungsten wire coil connected with a 220 volt circuit. The Pyrex tips had previously been polished optically plane. A small capillary hole extended through the tip downward from the center of its surface. After the surface of the tip became coated, it was allowed to cool in the vacuum and was quickly transferred to the contact angle cell just prior to use. Excellent mirror surfaces were obtained with both silver and gold.

Method for Observing and Measuring Contact Angles.—The method adopted for producing and measuring contact

(1) The material presented in this paper is from a dissertation submitted by Paul H. Cardwell to the Horace H. Rackham School of Graduate Studies of the University of Michigan in partial fulfillment of the requirements for the degree of Doctor of Philosophy, 1941. Original manuscript received May 21, 1941.

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