

The Imperial Academy of Sciences Vienna
ON *from the Author*

CERTAIN PRODUCTS OF DECOMPOSITION

OF THE

FIXED OILS IN CONTACT WITH SULPHUR.

BY

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XXIV.—*On certain Products of Decomposition of the Fixed Oils in contact with Sulphur.* By THOMAS ANDERSON, Esq. M.D., F.R.S.E., *Lecturer on Chemistry, Edinburgh.*

(Read 19th April 1847.)

Numerous researches have established as a general rule that the products of the decomposition of organic substances vary with the circumstances of the experiment, and the nature of the agents under the influence of which it is performed. If, for instance, we examine the action of heat alone, we find it causing a set of decompositions specially characterised by the evolution of carbonic acid, formed by the union of part of the carbon of the substance with the whole or part of its oxygen; and this action is rendered more definite, and the number of the products circumscribed by all circumstances facilitating the formation of carbonic acid, such as the presence of a base, which will even cause its evolution when heat alone is incapable of producing decomposition. Acids, on the other hand, have a precisely opposite effect, they, in some instances, altogether prevent the formation of carbonic acid, and cause the oxygen to exert its action on the hydrogen of the compound, and to eliminate one or more atoms of water which do not generally exist ready formed in it.

In these particular instances decomposition takes place at the expense of the constituent atoms of the compounds themselves, the extraneous substances serving merely as disponents to the oxidation, in the one case of part of their carbon, in the other of their hydrogen; but there is another class of agents which, besides eliminating one or more substances, are capable at the same time of entering into union with the residual atoms, and forming a new derivative of the original compound. The best investigated of this class of agents are chlorine, bromine, nitric acid, and ammonia, the three former of which exert their action on the hydrogen, the latter on the oxygen of the substance, and form compounds the complete investigation of which is important, not merely in a purely chemical point of view, but also from the light which they seem likely to throw on the general question of the atomistic constitution of matter. In fact, the great object of the researches of organic chemistry at the present moment is that of developing the relations which the individual atoms bear to the molecules of their compound, by a knowledge of which we hope eventually to arrive at some definite conclusions with regard to the mode in which the elementary atoms are grouped together in a complex molecule. Almost all the scanty information which we possess on this subject has been derived from investigating the products of the action of different agents upon organic substances; and it is sufficiently obvious, that the more varied the circumstances, and numerous the points of view under which these re-

actions can be examined, so much the more likely are we to arrive at definite results.

It was the consideration of these points which led me to undertake an investigation into the nature of the action of Sulphur in the free state upon organic compounds, a subject hitherto totally uninvestigated, unless we except the curious researches of ZEISE* on the simultaneous action of ammonia and sulphur upon acetone, which yields a variety of remarkable products, the properties of which he has described, without however determining their constitution. The results at which I have already arrived in these researches are contained in the following pages. They are, however, to be considered only as the commencement of the investigation; and I am desirous of submitting them to the Society even in their present very imperfect state, as it is impossible to fix a period within which a series of researches, surrounded by so many difficulties, can be completed. No one who has not been specially occupied with such experiments can have any conception of the numerous sources of annoyance which they present, and of the expenditure of time and labour which is necessary for their performance. Indeed, I have more than once felt inclined altogether to abandon a subject occupying so much time in proportion to the results obtained, and the completion of which is further protracted by the nauseous odour of the compounds, which is so disgusting that it is impossible to pursue the investigation for any length of time continuously.

At the commencement of these researches I endeavoured to examine the action of sulphur upon some of the simpler organic compounds, in the hope of arriving at results of corresponding simplicity. My expectations, however, were disappointed, and I was obliged to have recourse to the fixed oils, on which sulphur has been long known to exert an action; the product obtained by heating together olive oil and sulphur until an uniform balsam-like substance was formed, having been employed in medicine by the older physicians under the name of the Balsam of Sulphur.

The phenomena which manifest themselves during the mutual action of Sulphur and a Fixed Oil are these:—At the first application of heat the sulphur melts and forms a stratum at the bottom of the oil; but as the temperature rises it slowly dissolves, with the formation of a thick viscid fluid of a dark red colour. As the heat approaches that at which the oil undergoes decomposition when heated alone, a violent action takes place attended by the evolution of sulphuretted hydrogen in such abundance that the viscid mass swells up and occupies a space many times its original bulk. If at this point the mixture be allowed to cool, it concretes into a tough sticky tenaceous mass, adhering strongly to the fingers, and having a disagreeable sulphureous odour; if, however, the heat be

* Förhandlingar vid de Skandinaviska Naturforskarnes tredje möte, p. 303.

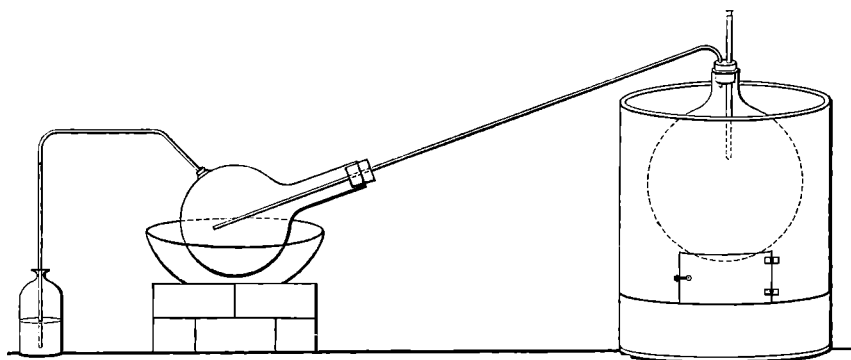
sustained, the frothing and evolution of sulphuretted hydrogen continue, and at the same time, an oil of a peculiar disgusting odour, resembling that of garlic, but more disagreeable, passes into the receiver.

In the investigation of the products of this action, the first and most essential step was to determine the particular constituents of the oil from which they are derived. In order to do this, it was necessary to examine separately the action of sulphur upon each of its components. I commenced, therefore, by making use of stearic acid, which can be readily obtained in a pure state: experiment however, shewed, that none of the peculiar products were derived from it; for when mixed with half its weight of sulphur and distilled, mere traces of sulphuretted hydrogen were evolved, and the products were identical with those obtained from the unmixed acid. The nauseous smelling oils being then obviously derived either from the oleic acid, or the glycerine of the oil, I prepared a quantity of pure oleic acid, by the decomposition of the ethereal solution of the oleate of lead. This, when mixed with half its weight of sulphur, and distilled in a capacious retort, underwent decomposition precisely as the crude fixed oil did; sulphuretted hydrogen was developed in great abundance, and the product of the distillation could not be distinguished from that which I had previously obtained. I was unable to obtain glycerine in sufficient quantity to make a separate investigation of the products of its decomposition, but these must also be peculiar, as I could not distinguish the presence of acroleine during any period of the distillation of an oil with sulphur.

The product of the distillation of oleic acid was in the form of a reddish-brown oil, having an extremely nauseous odour, in which that of sulphuretted hydrogen was apparent. When rectified, this sulphuretted hydrogen was driven off, and the first portions which distilled were perfectly transparent and colourless. As the process continued, however, the products became gradually darker in colour, and the last portions which distilled became semisolid on standing, from the deposition of a quantity of white crystalline plates. These were separated by filtration through cloth, expressed strongly, and purified by successive crystallizations from alcohol, until they were entirely free from smell and colour. The product was then in the form of white pearly scales, which possessed acid properties, and were totally insoluble in water; they were not therefore sebacic acid, no trace of which could be discovered among the products; but, on the contrary, possessed all the properties of margaric acid. These crystals were obtained from quantities of oleic acid, prepared at different times, and with the greatest possible care, and must have been formed during the decomposition. In order, however, to set this point at rest, some of the same oleic acid was distilled alone, when abundance of sebacic acid was obtained, and the latter portions of the rectified product did not deposit any crystals on cooling, but remained perfectly fluid. As this solid acid is produced only in comparatively small quantity, and

I was unable to obtain enough of oleic acid, I made use, in preparing it on the large scale, of pure almond oil, which, according to SCHÜBLER and GASSEROW, is entirely free of margarine. The oil which I employed was expressed specially for these experiments, at a temperature slightly above 32° ; and in order to satisfy myself of the absence of margaric acid in the products of its ordinary decomposition, a quantity was distilled alone, and the product rectified. The latter portions being collected apart did not deposit margaric acid; and this I have also found to be the case with the ordinary almond oil of commerce, in the expression of which a moderate degree of heat is employed.

In distilling the oil and sulphur on the large scale, it became impossible to perform the process by the simple admixture of the substances, the frothing being so great as inevitably to expel the materials from the retort. After a trial of various methods, I found it most convenient to employ the apparatus, of which this is a sketch. The oil was introduced into a large glass balloon, to the mouth



of which two tubes were adapted, one descending to near the middle, and furnished with a cork at the upper end, the other which constituted the neck of the distilling apparatus passed into a tubulated receiver, kept cold by immersion in water or ice. To the tubulature, a doubly bent tube was affixed, which descended into a vessel of alcohol, for the purpose of retaining any of the more volatile portions which might be carried over by the rapid current of sulphuretted hydrogen. The heat must be applied by means of an open charcoal fire, and the furnace should be so constructed, that the fire may be rapidly withdrawn in the event of the action becoming too violent. It is very desirable too, that the balloon should go down into the furnace, so that it may be entirely surrounded by hot air. The oil is introduced into the balloon, of which it must not occupy more than a fifth, or a fourth at most, along with a few small pieces of sulphur, and heat is gradually applied. So soon as effervescence commences, the cork of the small tube is withdrawn, and a small piece of sulphur is introduced; and this is continued gradually, so as to keep up an uniform action. A dark reddish-brown oil passes

into the receiver, and at the same time sulphuretted hydrogen passes in torrents through the alcohol; it there deposits a certain quantity of oil, and on escaping, may be kept burning during the whole operation, with a flame eight or nine inches high. The principal difficulty of this process consists in regulating the heat, so as to keep up a steady action. If the heat be allowed to fall, the contents of the balloon become so viscid, as inevitably to boil over; and at the same time too high a temperature causes the whole action to go on with excessive violence. I have generally operated on quantities of three pounds, each of which requires a complete day for its distillation, during which time the operator must never leave it, but constantly attend to the regulation of the heat, and the gradual addition of sulphur in small quantities. When a quantity equal to about half the oil employed has distilled over, the remaining mass becomes excessively viscid; and just at this point the balloon frequently cracks, the contents escape, and the whole catches fire, and blazes off with a bright yellow flame, and smell of sulphurous acid.

The product of this distillation, which exactly resembled that of the pure oleic acid, was rectified, and the crystals which deposited from the latter portions were expressed and purified by successive crystallizations in alcohol. They then presented all the characters of margaric acid, and gave the following results of analysis:—

I.	{	5·275 grains of the acid gave	
		14·558 carbonic acid, and	
		5·919 ... water.	
II.	{	6·358 grains of the acid gave	
		17·578 carbonic acid, and	
		7·212 water.	

Which gives the following results per cent.—

	Experiment.		Calculation.		
	I.	II.			
Carbon,	75·27	75·40	75·55	C ₃₄	2500·0
Hydrogen, . . .	12·51	12·66	12·59	H ₃₄	425·0
Oxygen,	12·22	11·94	11·86	O ₄	400·0
	100·00	100·00	100·00		3325·0

These results agree completely with the formula for margaric acid, and were farther confirmed by the analysis of its silver salt and ether.

4·643 grains of the silver salt gave 1·325 of silver = 28·53 per cent.

7·926 grains of the silver salt gave 2·284 of silver = 28·70 per cent.

The calculated result for margarate of silver gives 28·65 per cent.

The ether was prepared in the usual manner, by dissolving the acid in absolute alcohol, and passing dry hydrochloric acid gas through the solution. The product, which possessed all the properties of margaric ether, gave the following results of analysis :

$$\left\{ \begin{array}{ll} 5.596 \text{ grains of the ether gave} \\ 15.662 & \text{carbonic acid, } \cdot \\ 6.399 & \text{water.} \end{array} \right.$$

	Experiment.		Calculation.	
Carbon,	. . 76.33	76.51	C_{38}	2850.0
Hydrogen,	. 12.70	12.74	H_{38}	475.0
Oxygen,	. 10.97	10.79	O_4	400.0
	<hr style="width: 50%; margin: 0 auto;"/> 100.00	<hr style="width: 50%; margin: 0 auto;"/> 100.00		<hr style="width: 50%; margin: 0 auto;"/> 3725.0

These analyses establish, in a satisfactory manner, that the acid produced was margaric acid. It is scarcely possible, however, in the present state of the investigation, to give anything like a rational explanation of the mode in which it is here formed. Its production from oleic acid has been already observed by LAURENT as the first product of oxidation by nitric acid; but the action of sulphur is certainly of a very different character, and cannot be considered as bearing any analogy to that of an oxidising agent. The quantity of margaric acid produced does not appear to be constant, but varies with the rapidity of the distillation, and is always most abundant when it is slowly performed.

The oil which distils previous to and along with the margaric acid, and constitutes by far the most abundant product of the action of sulphur upon oleic acid and oil of almonds, is a very complex substance, and contains some of its constituents in very small proportion. On this account I found it necessary to prepare it in very large quantity; and in doing so I abandoned the use of almond oil and employed linseed oil instead, which is a much cheaper substance, and yields the same fluid products. When the product of the action of sulphur is carefully rectified, the first portions which pass over, are perfectly transparent and colourless, highly limpid and mobile, and boil at the temperature of 160° Fahr. Only a small quantity, however, passes at this temperature, and the immersed thermometer gradually rises without indicating any fixed boiling point for the fluid. My first attempts to purify this oil, and separate it into its various constituents, did not afford any satisfactory conclusions. Numerous analyses of the more volatile portions were made without obtaining comparable results, although all indicated the presence of carbon and hydrogen nearly in the proportion of equal atoms. The following are the details of three of these analyses:—

I.	{	4·657 grains of the most volatile oil gave
		12·688 ... carbonic acid, and
		5·127 water.
II.	{	5·501 grains of an oil less volatile than the preceding gave
		15·762 ... carbonic acid, and
		6·292 water.
III.	{	4·191 grains of another portion of oil gave
		12·185 carbonic acid, and
		4·720 ... water.

Which correspond to the following results per cent. :

	I.	II.	III.
Carbon,	75·03	78·79	79·95
Hydrogen, .	12·20	12·72	12·75

All these oils, when treated with fuming nitric acid, yielded an abundant precipitate of the sulphate of barytes; but as the results of the combustion were not constant, no quantitative determination was made.

The action of precipitants, however, upon this oil, afforded a more satisfactory method of obtaining some of its constituents. It gives, with corrosive sublimate, a bulky white precipitate, and with bichloride of platinum, a yellow compound, the characters of which vary slightly, according as it is prepared from the more or less volatile portion of the oil. Nitrate of silver and acetate of lead, mixed with the alcoholic solution of the oil, produce only a slight cloudiness, but on boiling the solutions, the sulphurets of silver and lead are deposited.

The Mercury Compound. In order to obtain this substance in the pure state, the oil was dissolved in alcohol, and an alcoholic solution of corrosive sublimate added. The precipitate which fell was collected on a filter, and washed with ether, until the oil was thoroughly extracted, for which purpose a considerable quantity of ether is required. It is then boiled with a large quantity of alcohol, which dissolves a part of it, and the solution being filtered hot, allows the compound to deposit, on cooling, in the pure state. It is then in the form of a white crystalline powder, having a very fine pearly lustre, and exhibiting under the microscope crystals of a very peculiar form. They are six-sided tables, two opposite angles of which are rounded off, so as to give them a very close resemblance to the section of a barrel. It possesses, even after long-continued washing with ether, a peculiar slight sickening smell, which becomes more powerful on heating, and its powder irritates the nose. It is insoluble in water, which moistens it with difficulty. It requires several hundred times its weight of boiling alcohol for solution, and is almost entirely deposited, on cooling, in microscopic crystals. In ether, it is almost insoluble. When heated, it is decomposed with the evolu-

tion of a peculiar nauseous smelling oil. The sparing solubility of this compound in alcohol renders its preparation in sufficient quantity for analysis an extremely tedious process, and I have sought in vain for a more abundant solvent. The only substance which I have found capable of taking it up in larger quantity, is coal-tar naphtha, but its employment is inadmissible, as the best which can be procured is an extremely impure substance, and the crystals of the compound deposited from it always acquire a rose or violet tint from some of its impurities. Oil of turpentine likewise dissolves it, but not more abundantly than alcohol.

By many successive solutions in alcohol, I obtained enough of this substance for an analysis, of which the following are the results:—

{	12·302 grains, dried in vacuo, gave
	6·592 ... of carbonic acid, and
	3·018 ... of water.

8·061 grains, deflagrated with a mixture of nitre and carbonate of soda, gave 7·297 grains of sulphate of baryta = 1·0067 = 12·48 per cent. of sulphur.

The mercury and chlorine were determined together by mixing the substance with quicklime, and introducing the mixture into a combustion tube. The end was then drawn out into an elongated bulb, into which the mercury sublimed, and which was afterwards cut off, dried in the water-bath, and weighed, both with and without the mercury; the chlorine was determined in the usual way from the residue in the tube.

9·958 grains gave 5·976 mercury = 60·01 per cent., and 4·310 grains chloride of silver = 10·67 per cent. of chlorine.

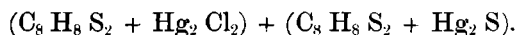
5·797 grains gave 2·409 of chloride of silver = 10·25 per cent. of chlorine.

These results correspond closely with the formula $C_{16} H_{16} S_5 Hg_4 Cl_2$, as is shewn by the following comparisons:—

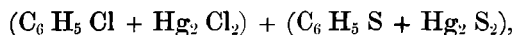
	Experiment.		Calculation.			
	I.	II.				
Carbon . . .	14·61	...	14·46	C_{16}	1200·0	
Hydrogen . . .	2·72	...	2·42	H_{16}	200·0	
Mercury . . .	60·01	...	60·32	Hg_4	5003·6	
Chlorine . . .	10·67	10·25	10·67	Cl_2	885·3	
Sulphur . . .	12·48	...	12·13	S_5	1005·8	
	100·49	...	100·00		8294·7	

It is sufficiently obvious that the formula $C_{16} H_{16} S_5 Hg_4 Cl_2$ cannot be supposed to represent the rational formula of this substance. On the contrary, the remarkable analogy between its properties and those of the mercury compound of sulphuret of allyl appear clearly to indicate a similarity in their chemical constitution,—a similarity which, as we shall afterwards see, is borne out by the properties of the platinum compound. I consider this substance to contain an or-

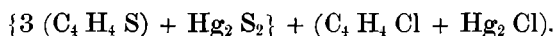
ganic sulphuret, analogous to sulphuret of allyl, the constitution of which must be represented by the formula $C_8 H_8 S_2$, to which I give the provisional name of Sulphuret of Odmyl (from *ὀδμῆν ὄδορ*), and that the rational formula of the mercury compound is—



On contrasting this with the formula of the allyl compound, which is—



two important points of difference are apparent, namely, that in the new compound we have the sulphuret, and not the chloride, of the base in union with corrosive sublimate, and the presence of subsulphuret in place of sulphuret of mercury in the second member of the compound. It is even possible to approximate more closely the formulæ of the allyl and odmyl compounds, by assuming the sulphuret of odmyl to be represented by $C_4 H_4 S$; in which case, the mercury compound becomes:—



This formula is, however, incompatible with its reactions, as it involves the presence of calomel in the compound. Treatment with caustic potash, however, shews that this is not the case; as it immediately becomes yellow, from the separation of oxide of mercury, while the black suboxide would have been formed had calomel been present.

When a current of sulphuretted hydrogen is passed through the mercury compound suspended in water, it becomes rapidly black, a peculiar smell is observed, along with that of sulphuretted hydrogen, and, by distillation, an oil passes over, which is obtained floating on the surface of the water. It is perfectly transparent and colourless. Its smell is peculiar, and resembles the nauseous odour developed by crushing some umbelliferous plants. When dissolved in alcohol, it gives, with corrosive sublimate, a white precipitate, soluble in hot alcohol, from which it is deposited in crystals precisely similar to those from which it had been originally separated, and, with bichloride of platinum, a yellow precipitate, slightly soluble in hot alcohol and ether. This oil is, in all probability, the sulphuret of odmyl $C_8 H_8 S_2$, but the small quantity in which I have been able to obtain it, has prevented my performing any analysis of it.

The Platinum Compound. When a solution of bichloride of platinum is added to the alcoholic solution of the crude oil, a yellow precipitate makes its appearance, which does not fall immediately, but goes on gradually increasing for some time, precisely as is the case with the allyl compound. The properties of this precipitate are not, however, perfectly constant, but vary according to the portion of the oil employed to yield it. That obtained from the more volatile portion has a fine sulphur-yellow colour, but the less volatile oil gives an orange precipitate. It is

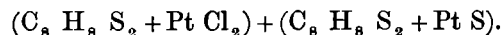
insoluble in water, sparingly soluble in alcohol and ether. When heated it becomes black, an oil is evolved smelling exactly like that obtained from the mercury compound and sulphuret of platinum is left behind, which requires a high temperature to drive off all its sulphur, and leaves metallic platinum as a silver-white mass. When treated with hydrosulphuret of ammonia, it is converted into a brown powder, exactly like that obtained under similar circumstances from allyl.

The analysis of the yellow compound has not hitherto given results of a satisfactory character. I have found the amount of platinum to oscillate between 43·06 and 49·66 per cent. The former of these was obtained from the most volatile oil, the latter from that which boiled between 300° and 400° Fahr., and intermediate results were obtained at intermediate temperatures. The results obtained from the oil which boiled at a high temperature were remarkably constant; thus I have found, in different experiments, 49·00, 49·51 and 49·66 per cent. of platinum, which appear to indicate the presence of some compound of rather sparing volatility. The precipitate obtained from the most volatile oil appears to be that corresponding to the mercury compound which has just been described. Of it I have been able only to perform a very incomplete analysis, which is insufficient to establish its constitution, especially as it is impossible to ascertain whether it is a homogeneous substance. As the results, however, approximate to a formula analogous to that of the mercury compound, I give the details, such as they are.

{	9·155	grains of the platinum compound gave
	7·474	carbonic acid, and
	3·294	water.

5·701 grains gave 2·455 grains of platinum, = 43·06 per cent.

These results approximate to a formula similar to that of the mercury compound :—viz.



Experiment.		Calculation.		
Carbon, . . .	22·26	20·83	C ₁₆	1200·0
Hydrogen, . .	3·99	3·47	H ₁₆	200·0
Platinum, . .	43·06	42·84	Pt ₂	2466·6
Chlorine,	15·38	Cl ₂	885·3
Sulphur,	17·48	S ₈	1005·8
...	...	100·00		5757·7

The analogy which those substances bear to allyl is exceedingly interesting, as shewing the possibility of forming, by artificial processes, substances similar in constitution to so remarkable a compound, which is not a product of decomposition, but exists ready formed in a variety of different vegetables, where it must

obviously be produced under circumstances very different from the artificial substance; for allyl cannot exist at all at a high temperature, and is entirely decomposed at, or even below, its point of ebullition. Unfortunately, however, the examination of this substance is much complicated by the necessity of examining its compounds in place of itself. Had it been possible to separate it directly from the crude oil, the determination of its constitution and that of its compounds would have presented comparatively little difficulty, and been arrived at with much less labour than that expended upon the imperfect details I have been able to accumulate. Another point worthy of observation, is the total alteration of the products of decomposition of oleic acid produced by the presence of sulphur; no sebacic acid, and, in fact, none of its ordinary products being evolved, although all the substances produced contain carbon and hydrogen in the proportion of equal atoms, just as they exist among the ordinary products,—a circumstance which, taking into consideration the abundant evolution of sulphuretted hydrogen, we certainly should not have anticipated.

The oil which remains after the separation of the mercury compound, likewise contains sulphur as one of its constituents; but I have not yet had time to commence the investigation of this part of the subject. The discussion of it, as well as various other points connected with the compounds already described, I hope to make the subject of a future communication.