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ART. LV.—*On Endothermic Decompositions obtained by Pressure. Second Part. Transformations of Energy by Shearing Stress*; by M. CAREY LEA.

OF the relations which exist between two forms of energy, mechanical and chemical, very little if anything is known. In the second volume of his *Lehrbuch*, Ostwald remarks that as to these relations "almost nothing" is known.*

There are certain familiar cases in which mechanical energy may seem at first sight to be converted into chemical energy. The fulminates, iodimide, and other substances explode by shock. But it is hardly necessary to remark that all such reactions are exothermic and need an external impulse only, to start them—if this impulse were not needed such compounds could not exist at all. Were such reactions taken as true transformations of energy an absence of due relation between cause and effect would be involved. For the shock that suffices to explode a grain of fulminate will equally explode a ton. The faint spark that will explode a grain of gunpowder will also explode a magazine.

Present opinion holds undoubtedly that no true transformation of mechanical into chemical energy is known. Most text books do not consider the question at all. But Dr. Horstmann in the volume of theoretical chemistry which forms part of the last German edition of Graham Otto's *Chemistry*, discusses the

* "Andererseits ist von der Verhältnis zwischen mechanischer und chemischer Energie, fast nichts bekannt." A few lines below, this remark is repeated with emphasis. *Lehrbuch*. 2d German ed., vol. ii, p. 12.

matter. His views are so much to the point that I shall translate a few sentences, putting in italics the statements to which I would specially refer.

"We must consequently admit that through a rough mechanical attack the molecular structure of certain chemical compounds can be disrupted and destroyed. This will certainly be possible only for compounds in whose molecules the arrangement of the atoms does not correspond to a stable equilibrium and in which therefore the chemical energies themselves are already striving to form simpler and more stable compounds out of the constituents of the existing substance. *For it cannot be admitted that actual chemical changes can be brought about by a mechanical impulse.*" (l. c., p. 350).

In another chapter he says with equal distinctness:

"By mechanical means alone no reaction against the force of chemical energy can be brought about. By a shock or blow the molecular structure of chemical compounds can indeed be so far loosened that free play is given to chemical forces; but against these forces we cannot by mechanical means separate the atoms nor combine them in a definite way." (p. 594).

These expressions of a distinguished chemist will sufficiently indicate what has been up to the present time the opinion of chemists as to the possibility of transforming mechanical energy into chemical.

In the first part of this paper I believe I have been able to show in a qualitative way the production of true endothermic reactions by mechanical force. In the present part I hope to show an increased number of such reactions and in one case to exhibit actual quantitative results, at least so far as to obtain the product of the transformation in weighable quantities.

In the first part decompositions were described that were brought about by *simple pressure*. Compounds formed by exothermic reactions, and therefore requiring expenditure of energy to break them up, were decomposed. The investigation might probably have been made to include a still larger range of substances. But it was found that the efficiency of pressure was so enormously increased by the addition of shearing motion, that decompositions requiring a force of hundreds of thousands of pounds with pressure alone, could be effected by the mere strength of the hand when shearing stress was used. More than this, decompositions which enormous pressures failed to effect, readily took place under the action of shearing stress.*

* It would not have been difficult to obtain much greater pressures than those described in the first part of this paper. This could be effected by means of the differential screw. I had planned for a screw with threads of 40 turns in 10 inches

(I)

It was mentioned in a previous paper on the decomposition of the silver haloids by mechanical force that when silver chloride was sharply ground for some time in a mortar, both the pestle and mortar became covered with a deep purple varnish of silver photochloride, thus indicating a partial reduction to subchloride. It has since proved that there is no more effectual method than this of applying shearing stress and that in this way a number of quite stable chemical compounds formed by exothermic reactions can be broken up. The mortar and pestle should be very solid and of unglazed porcelain. With metal, there would be danger of action between the metal and the substance and with agate mortars sufficient force cannot well be applied. In many cases success depends on the exertion of great pressure on the pestle. It is also absolutely essential that the quantity of material acted upon should be small. When a larger quantity is employed the particles slip or roll over each other and thus escape the action of the stress. It is no doubt for this reason that the very remarkable results which can be obtained in this way have hitherto escaped attention.

A small quantity, a few decigrams, of the substance having been placed in the mortar the first thing is to spread it in a thin uniform coat over the bottom and part of the sides. The pestle is then to be rotated with the utmost force that can be exerted.

Sodium Chloraurate.—The salts of gold are particularly well adapted to this examination as the reduction is complete

and 39½ turns in 10 inches respectively. The mechanical efficiency of such a screw is that of one having 320 turns to the inch if such a thing were practicable, at the same time that a thoroughly strong construction can be obtained. The massive steel nut to advance ¼ of an inch would require 40 full turns of this screw.

This arrangement compares as follows with that previously employed. In it to cause the vise jaws to approach by 1 inch required that the point of the lever at which the force was applied should pass through a space of 113·1 feet: this relation, 1 inch to 113·1 feet or 1:1357·2 gives the measure of the efficiency of the instrument.

With the double screw, on the other hand, to cause the nut to advance ¼ of an inch the end of the lever (2 feet long) must pass through a space of 500 feet or in the proportion of 1 inch to over ¼ of a mile. The circumference described by the lever being approximately 12½ feet and the screw requiring 40 turns to advance the nut ¼ of an inch we get the proportion of 1 inch to 4,000 feet, or 1 to 48,000, which is the measure of the efficiency of such an instrument. Therefore, supposing two men to pull on the end of the lever each with a pull of 100 lbs. the pressure exerted on the nut (disregarding loss by friction) would be 9,600,000 lbs., which could be doubled by using a 4-foot lever.

Such a combination is quite practicable, the only real difficulty being to obtain sufficient solidity of construction to resist the strain. I had made drawings for this instrument, but gave it up in consequence of observing the enormously greater efficiency of shearing stress as a means of transforming mechanical into chemical energy.

and the gold appears in the metallic state so that it can be weighed and the exact amount of reduction can be fixed. It will be seen by (3) below that it may amount to as much as over 4 per cent of the gold present.

(1) Two or three decigrams of chloraurate with a moderate trituration left 1.8 milligram of metallic gold. Under the action of the pestle the yellow color of the salt gradually deepened to an olive shade. When water was poured on, the undecomposed salt dissolved, leaving the gold as a delicate purple powder. The color of the gold being purple instead of the more usual brown shade explains the olive color just mentioned, yellow and purple combining to form olive.

(2) Half a gram of the salt was taken. This specimen was more neutral than the preceding and was therefore more easily reduced. Half an hour's trituration had for effect the reduction of 9.2 mgs. of gold.

(3) A similar treatment of the same quantity of chloraurate resulted in the separation of 10.5 mgs. of gold.

These may seem at first somewhat small proportions. But it is to be recollected that the force is necessarily applied at a disadvantage and that the equivalent in work of chemical affinity is always very large. In the present case the figures are as follows: Thomsen found as the heat equivalent for the combination of gold with chlorine to form auric chloride 28.8 great calories. Taking the atomic weight of gold as 197, we find that one gram of gold in forming auric chloride disengages 115.7 small calories or water-gram-degrees, whose equivalent, taking Rowland's determination, is 49,288.2 gram-meters corresponding to 4.83×10^9 ergs or 483 joules.

The small quantity of gold reduced in (3), 10½ milligrams, would by conversion to auric chloride generate 1.215 water-gram-degrees of heat whose equivalent in work is 518 gram-meters. As heat is a degraded form of energy such an actual transformation without loss to a higher form would be impossible. It is more correct to say, therefore, that the amount of energy which would raise 518 grains to the height of one meter can be transformed into the same amount of heat, 1.215 water-gram-degrees, as is evolved by 10.5 mgs. of gold by conversion into auric chloride. Consequently this work, 518 gram-meters represents the amount of mechanical energy transformed into chemical energy in operation [3].*

It does not appear that in effecting these reactions and the others which remain to be described, mechanical energy under-

* The amount of energy required would in fact slightly exceed this as the thermochemical equivalent of formation of sodium chloraurate would slightly exceed that of auric chloride. For the chloraurate I do not find a determination, but preferred to use this salt in the operation as being both more stable and more neutral, than auric chloride.

goes an intermediate conversion into heat. Rapid movements are not needed, what is required is strong pressure with movement, but this need not be rapid. Nor does the mortar or the pestle become sensibly warm. The operation does not need to be continuous but may be broken up with any number of intervals. But a decisive conclusion can be drawn from those cases in which decompositions are effected in this way that *cannot be produced by heat*. For example, in the next instance to be mentioned there is a partial reduction of corrosive sublimate to calomel. By heat, corrosive sublimate sublimes unaltered and the same is true of mercurous chloride. The three silver haloids fuse unchanged at a red heat. The same conclusion can be drawn from other reactions.

These results were obtained in an atmosphere absolutely free from dust so that the reducing action of this substance was completely excluded.

Mercuric Chloride.—A specimen which after lightly powdering did not darken in the least with ammonia, was trituated in the manner just described with several intervals, in all for 15 minutes. It then became gray in a very striking way when moistened with ammonia.

This is a very interesting reaction. In the first part of this paper it was mentioned that mercuric chloride could be subjected to a pressure of about 70,000 atmospheres absolutely without change. It appears, however, that a pressure amounting to less than a hundred pounds causes decomposition when combined with movement, showing the enormously greater efficiency of shearing stress as compared with simple pressure. Not only this but as just mentioned shearing stress produces decompositions which heat is not competent to effect.

Mercurous Chloride.—When calomel was sharply trituated in a mortar it first became yellow and then blackened without difficulty.

Turpeth Mineral, $3\text{HgO} \cdot \text{SO}_3$.—Reduces rather slowly.

Mercuric Oxychloride, $2\text{HgO} \cdot \text{HgCl}_2$, obtained by precipitating corrosive sublimate by potash acid carbonate, exhibited the following reaction. Its brownish purple color by light grinding became lighter and then when strong force was used it blackened with remarkable ease.

Mercuric Iodide shows a trace of blackening.

Mercuric Oxide.—This substance yields much more readily to trituration than to simple pressure. Especially on the sides of the mortar it was quite blackened. The layer of material must be quite thin otherwise little effect is produced.

Platinic Chloride.—Gradually darkened in a very marked way, finally becoming blackish.

Ammonium Platinichloride gave same result.

Silver Tartrate.—When spread in a very thin skin over the mortar each sharp stroke of the pestle left a black line behind it. This is a strong contrast with the complete resistance of this substance to simple pressure.

Silver Carbonate.—Action similar.

Silver Citrate.—Blackens very easily.

Silver Oxalate.—At least as easily.

Silver Arsenate.—Nearly as easily.

Silver Sulphite.—Effect visible in five minutes and gradually increasing. Very well marked.

Silver Salicylate.—No silver salt appears to be so easily reducible as this. Every sharp stroke of the pestle leaves a brown mark behind it.

Silver Orthophosphate.—Affected easily. After the phosphate has been a good deal reduced the unchanged part may be dissolved out with ammonia. The black residue after washing readily dissolves in dilute nitric acid and the solution gives a white cloud with hydrochloric acid.

Potassium Ferridcyanide.—A crystal of the pure salt sharply ground in a mortar becomes in portions brown and in others blue. The quantity used must, as indeed in all of the above cases, be small, one or two decigrams. If a little distilled water be added an insoluble blue powder is left behind and the solution formed strikes a blue color when added to one of ferric alum. This indicates that the decomposition is two-fold. The experiment is quite a striking one and the result is easily obtained.

(II)

This form of mechanical force, shearing stress, may be applied to effect endothermic change in other ways. A very simple, and at the same time very efficient, method is that of pressure with a glass rod. Pure strong paper is to be imbued with a solution of the substance, if it is soluble, or if not, it is to be made into a paste with water and then applied with a brush. The paper is to be then very thoroughly dried and is to be laid upon a piece of plate glass. Characters are to be marked on it with the end of a glass rod that has been rounded by heat, using as much pressure as is possible without tearing the paper.

More than twenty years ago I was able to show that marks made in this way on sensitive photographic films could be developed, as an invisible image had been impressed. That, however, is a somewhat different matter from actual and visible decomposition following each stroke of the rod, a result which may be obtained with various salts of gold, mercury, silver and other metals.

Potassium Ferridecyanide.—Pure paper was imbued with a dilute solution of this salt. After thorough drying it was laid on a glass plate and marks were made with a glass rod in the manner just described. These marks were immediately visible and when the paper was plunged into dilute solution of ferric ammonia alum or of ferric chloride they became dark blue. It is probable that the decomposition here effected was twofold (see above).—The *nitroprussides* appear to be much more stable than the ferridecyanides. When sodium nitro prusside paper was treated with pressure, followed by appropriate reagents, no indications of decomposition were obtained.

Auric Chloride.—Paper imbued with a solution of auric chloride and marked in the manner described was thoroughly soaked in water to remove, as far as possible, the rest of the gold salt. The marks were very distinct and gradually gained with time. Color dark purplish gray.

Platinic Chloride.—After drying and marking, the paper was thoroughly soaked in water and dried. The marks were very distinct, of a yellow color.

Ammonium Plutinichloride.—Marks very visible. Continued to slowly deepen, and in a few weeks were almost black.

Silver Carbonate.—The traces of the rod were brown. When the paper was placed in ammonia the carbonate dissolved, but the marks resisted the action of the ammonia and remained.

Silver Phosphate.—Action very similar to the preceding.

Silver Arsenate.—Similar action.

Silver Tartrate and Oxalate.—These salts gave analogous results to the preceding, but not so well marked. The carbonate phosphate and arsenate show this reaction best and about equally well. What is rather curious is that silver chloride does not exhibit a visible action.

Mercuric Oxide.—Paper imbued with a saturated solution of mercuric nitrate and then treated with solution of potash and dried shows this reaction very distinctly. Mercuric oxide appears to be quite sensitive to light.

Turpeth Mineral.—Mercuric sulphate was dissolved in water with the aid of sulphuric acid. Paper was soaked in the solution, allowed to become nearly dry and then washed. This paper showed the reaction very moderately, but the marks were brought out more strongly by immersion in ammonia.

Ferric Alum (ammonia).—Paper imbued with solution of this salt dried and marked was immersed in solution of potassium ferridecyanide. The marks came out blue showing that the ferric salt had undergone partial reduction.

It is easily conceivable that the action of shearing stress should be enormously greater than that of simple pressure. For it seems probable that pressure can only cause decomposition when the resulting product is more dense, has a greater specific mass, than the original substance. With shearing stress the case is altogether different. All matter is in a state of vibration and it is easily conceivable that the forcible friction of a hard substance may increase vibration in somewhat the same way as does a bow drawn over a stretched cord. Both the elasticity and the tension of the atoms themselves are vastly greater than those of any stretched cord so that the increased vibration may easily be sufficient to shatter the molecule.

The transformation of light, heat, and electricity into mechanical energy as well as the converse transformations are extremely familiar. That mechanical energy may be transformed into chemical energy is proved by the results in these papers described. The converse transformation, that of chemism into work, is in an industrial point of view by far the greatest chemical problem now waiting for solution. But it is by no means certain that such a transformation is practically possible. At least it seems probable that the improvement in our method of obtaining work from the chemism of carbon may be in the direction of substituting electricity for heat as the intermediary.