No. V. *On the action of Ozone on Carbon Monoxide;* by IRA REMSEN and MASE S. SOUTHWORTH.

One of the most remarkable examples of so-called non-saturated compounds is carbon monoxide. If we accept the hypothesis of constant valence, the compound CO must possess free affinities, or, as some chemists believe, the two affinities of the carbon-atom, which are not saturated by the oxygen atom, must exercise an influence upon each other. We can not explain this case by assuming that two carbon-atoms are joined together by two affinities each, for we know that the formula of carbon monoxide is CO, and not C_2O_2 or a higher multiple, and, accepting this formula, it is plain that we cannot assume a double union of carbon atoms in the compound.

If, on the other hand, we accept the hypothesis of variable valence, believing that the valence of an element depends upon circumstances, we shall look in vain for circumstances which, in the one case, can cause the bivalence, in the other the quadrivalence, of the carbon-atom. A difference in temperature certainly does not cause the difference in valence. The atom

* Annalen der Chemie, Suppl. VII, 218.

of carbon is quadrivalent toward oxygen at the ordinary temperature and under ordinary conditions. How otherwise shall we explain the formation of carbon dioxide in the processes of decay, fermentation, etc.? But the atom of carbon is just as positively quadrivalent at high temperatures.

The comparative ease with which carbon monoxide takes up chlorine appears to prove that it possesses free affinities. But if we accept this as a proof of the existence of free affinities in carbon monoxide, we have still better grounds for believing that free affinities are present in ethylene, for this gas combines with chlorine much more readily than carbon monoxide does. Still the view is commonly held that in ethylene the two carbon-atoms of the molecule are united by the mutual action of two affinities of each atom.

These considerations show that the nature of carbon monoxide is, as yet, but very unsatisfactorily understood. The first question which suggests itself is this: How far are we justified in considering carbon monoxide as a body possessing free affinities?

If we attempt to answer this question entirely without prejudice, we see that the principal experiment which is supposed to prove the existence of free affinities in carbon monoxide is the above mentioned experiment with chlorine. Oxygen does not combine with carbon monoxide at the ordinary temperature. This is readily understood, for, in order that the carbon monoxide and oxygen may combine by direct contact of the two substances, the oxygen-molecule must first be decomposed into its constituent atoms. An interesting experiment in this connection has been described by E. Ludwig,* who shows that carbon monoxide is oxidized by chromic acid at the ordinary temperature forming carbon dioxide. In this case carbon monoxide is active enough to separate one atom of oxygen from chromic acid and to employ it for the formation of carbon dioxide.

We have occupied ourselves with an experiment similar to that described by Ludwig, and have obtained a different and unexpected result. It appeared to us to be of interest to know whether, at the ordinary temperature, ozone has the power to transform carbon monoxide into the higher oxide. According to the views which are commonly held concerning the nature of the substances experimented upon, the transformation mentioned could be predicted with a tolerable degree of certainty. Particularly is this the case, if we consider the result of Ludwig's experiment, for usually ozone gives up its extra atom of oxygen with still greater readiness than chromic acid does. There is indeed no substance in the whole field of chemistry which furnishes us with a better means for obtaining

* Annalen der Ch. u. Pharm., clxii, 47.

a free atom of oxygen than ozone. If then we bring in contact with ozone a substance, which in turn is capable of taking up an atom of oxygen without itself undergoing change; which, indeed, possesses an attraction for oxygen, we are certainly justified in expecting to see the two substances act upon each other. But the experiment gave the unexpected result that ozone does not act upon carbon monoxide.

Two very careful experiments were performed. Pure carbon monoxide free of dioxide was first collected in a gasometer. This was then conducted from one side through three cylinders containing potassic hydroxide and lime-water into a flask. From the other side a current of oxygen was conducted through potassic hydroxide and lime-water, and then through a tube, in which the oxygen was converted into ozone, into the same flask. This flask was provided with a stopper having three holes. From the third hole a tube led to a cylinder containing lime-water; and this cylinder was connected with a final cylinder containing potassic hydroxide. Let us see what purposes the different parts of the somewhat complicated apparatus served. In the first place, the carbon monoxide was caused to pass through potassic hydroxide and lime-water in order to absorb every trace of carbon dioxide which might be present. The oxygen was treated similarly for a similar purpose. The ozone generator employed was that described by Wright* for use with the Holtz electrical machine, the best conditions being retained throughout the experiment for the working of the apparatus. The pure carbon monoxide and the ozonized oxygen were then caused to meet in the final flask, the inside of which was moist, as, for some unknown reason, ozone does not exhibit its oxidizing properties as well when dry as when moist. The mixture of the two gases, and any carbon dioxide which might have been formed, were then passed together into lime-water, contained in a cylinder, the lime-water being protected from the influence of the carbon dioxide of the air by the potassic hydroxide contained in the last cylinder.

Slow currents of carbon monoxide and oxygen were now passed through the apparatus, and, although the action was continued for a long time, not a trace of a precipitate could be detected in the last cylinder, containing lime-water. The strength of the gas-currents was frequently changed, but nothing brought about the expected result.

In view of the importance of the experiment we were not satisfied with this one form of it. As direct sun-light greatly facilitates the combination of carbon monoxide with chlorine, it seemed probable that it would be of service in causing the combination of the two gases under examination; and, accord-

* This Journal, vol. iv, July, 1872.

ingly, we repeated the described experiment with the following modifications: The final flask, above mentioned, in which the carbon monoxide and the ozone were brought together, was replaced by two large glass balloons, and these were placed in the direct light of the sun. Again slow currents of carbon monoxide and ozone were passed through the apparatus for hours, the rapidity of the currents being varied at different times.

In this case also we obtained only a negative result. We hence are in a position to assert positively that carbon monoxide is not oxidized by ozone.

If we now bear in mind that ozone acts destructively upon a great many saturated stable compounds, that one of the atoms of the ozone molecule has a great tendency to unite with other bodies, then the result of the above described experiments remains inexplicable. It shows at all events that carbon-monoxide itself, at the ordinary temperature, has no very great tendency to unite with oxygen, for, if our ideas in regard to the nature of ozone are correct, the conditions for such union were very favorable in our experiment.

We hope gradually to be able to experiment more fully upon this interesting subject with the object of collecting material which may enable us better to understand the nature of the so-called non-saturated compounds. We propose next to study the action of hydrogen peroxide upon carbon monoxide.

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