MONATOMIC IODINE AND MOLECULAR HYDROGEN*

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In 1884 Amato[1] showed that a mixture of hydrogen and chlorine in glass at $-12°$ could be exposed to the direct rays of the sun for hours without any appreciable reaction taking place, although the two gases will combine explosively if exposed to bright sunlight at ordinary temperatures.

About fourteen years later this suggested to Kastle and Beatty[2] the possibility that sunlight would cause hydrogen and bromine to react if the experiment were tried at a higher temperature. A number of qualitative measurements were made at 196°, the bulbs, containing an excess of hydrogen, being placed in the vapor of boiling orthotoluidine. In the dark the reaction is exceedingly slow, and practically negligible in a three-hour run. In the sunlight the reaction takes fairly rapidly. In the first series the bromine was practically all gone at the end of an hour, as judged by the eye. In the second series the bromine had reacted practically completely in ninety-five minutes. In the third series an estimated fifty per cent of the bromine reacted in the first fifteen minutes and practically all the rest in the next thirty minutes. In other words the bromine is converted practically completely into hydrobromic acid in from forty-five to ninety-five minutes.

The differences in the time for practically complete disappearance of bromine were due to differences in the intensity of the light. The bulbs in the third series were the only ones exposed the whole time to strong sunlight. During the first two series the sky was frequently overcast by thin, white clouds, which, of course, decreased the intensity of the light.

Kastle and Beatty say that there is some evidence that light causes hydrogen and bromine to react slowly even at 100°, and they promise a more extended and more quantitative study of this reaction. They also say that the influence of light on the combination of hydrogen and iodine at high temperatures will also be studied. So far as we can learn, this promised work has never been published.

There was every reason to believe that iodine would act like bromine and chlorine at still higher temperatures and experiments were therefore made by Mr. Morton to determine the effect of light on mixtures of hydrogen and iodine in glass containers at different temperatures. While there is a slight reaction in the dark at temperatures above 100°, perhaps due to the catalytic action of the walls, the amount of hydriodic acid formed in an eight-hour run in the dark is very small at temperatures up to 300°. Between 300° and 350° there is an enormous increase of reaction velocity. Using a 100-ampere arc we did not find any appreciable photochemical effect at any temperature. It made no difference whether we used all the light from the arc or whether the light was passed through a copper sulphate filter so as to remove the longer wave-lengths of the visible spectrum. This result was entirely unexpected. Iodine vapor absorbs light so strongly that we had anticipated a very large photochemical effect at a sufficiently high temperature.

To make the matter more interesting, we get an entirely different result if we use quartz vessels. Ultra-violet light makes hydrogen react with chlorine, bromine or iodine at ordinary temperatures. The fashionable thing would probably be to attribute this difference to the difference in the short-wave quantum; but this hypothetical explanation does not seem adequate. The real explanation seems to be that light in the visible spectrum does not activate hydrogen appreciably at any of the temperatures under consideration, while ultra-violet light does. For the present, it is generally believed that photochemically activated hydrogen and catalytically activated hydrogen are monatomic hydrogen, and we know that monatomic hydrogen reacts with chlorine, bromine or iodine at ordinary temperature.

If we assume, as seems justified, that a photochemically activated halogen is a monatomic halogen, we must conclude that monatomic chlorine reacts with molecular hydrogen at room temperature, that monatomic bromine reacts with molecular hydrogen at 196° and perhaps at 100°, and that monatomic iodine does not react with molecular hydrogen even at 350°. This is not without precedent, for monatomic hydrogen does not react with molecular nitrogen. On this basis we must assume that the reaction between hydrogen and iodine in the dark at 350° is really a reaction of thermally produced monatomic hydrogen with molecular [or monatomic] iodine. The rate of reaction of monatomic hydrogen with monatomic iodine must be practically the same as with molecular iodine because, otherwise, there would be a photochemical increase in the rate of reaction, which seems not to be the case.

These statements refer only to these monatomic elements at what might be called normal concentrations. At higher concentrations the behavior may be quite different. Thus Vincent[3] has shown that monatomic hydrogen will not reduce a potassium bichromate solution at the concentration which one gets at a platinum cathode, whereas monatomic hydrogen does reduce a potassium bichromate solution at the much higher concentration which one gets at a mercury cathode.

The general results of this paper are as follows:

1. Ultra-violet light activates hydrogen, while light of the visible spectrum does not do so appreciably.

2. We are justified for the present in calling photochemically activated or catalytically activated hydrogen, chlorine, bromine, or iodine, monatomic hydrogen, monatomic chlorine, monatomic bromine, or monatomic iodine, respectively.

3. Ultra-violet light causes hydrogen to react with chlorine, bromine or iodine at ordinary temperatures, and it is known that monatomic hydrogen reacts at ordinary temperatures with chlorine, bromine or iodine. It does not react with molecular nitrogen and ultra-violet light does not cause the formation of ammonia at ordinary temperatures.

4. Suitable light in the visible spectrum causes hydrogen and chlorine to react at room temperature, and hydrogen and bromine certainly at 196° and possibly at 100°. Light in the visible spectrum does not cause hydrogen and iodine to react even at 350°, a temperature at which the dark reaction proceeds quite rapidly. The dark reaction is undoubtedly due to thermally produced monatomic hydrogen.

5. Monatomic chlorine reacts with molecular hydrogen at ordinary temperatures; monatomic bromine reacts with molecular hydrogen at 196° and probably at much lower temperatures, though not appreciably at ordinary temperatures. Monatomic iodine does not react with molecular hydrogen to an appreciable extent even at 350°. While this was unexpected, it is not unique; for monatomic hydrogen does not react with molecular nitrogen under ordinary conditions.

6. Since the concentration of monatomic hydrogen which one gets at a platinum cathode is not sufficient to cause reduction of a potassium bichromate solution, whereas this reduction occurs with the concentration that one gets at a mercury cathode, the preceding generalizations apply only to what might be considered as approximately equilibrium concen-

trations of the monatomic elements and not necessarily to the concentrations corresponding to extreme over-voltage conditions.

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[1] Amato, *Gazz. chim. ital.*, **14,** 57 (1884).

[2] Kastle and Beatty, *Am. Chem. J.*, **20,** 159 (1898).

[3] Vincent, *J. Phys. Chem.*, **29,** 875 (1925).