	pH
No color	10.5 or less
Gray to faint blue gray	10.5–11.5
Blue gray to blue	11.5–12.0
Blue to blue green	12.0–12.5
Blue green to green	12.5–13.0
Green to black	13.0–14.0

In addition to its function as a test for the relative alkalinity of moist solids, the color reaction serves as a convenient method for distinguishing between the alkali triphosphates and diphosphates since the latter give no color. It also distinguishes between alkali tri- and di-arsenates and between alkali carbonates and bicarbonates. The reaction can be used to identify hydroquinone. Neither catechol nor resorcinal show similar color reactions. Finally, the reaction may be used as a convenient test to indicate the presence or absence of moisture or water of hydration in an alkaline salt. The anhydrous salts show no color on grinding with hydroquinone; the color appearing only after the mixture stands over water. Hydrated salts show immediate color on grinding.

COLGATE UNIVERSITY
HAMILTON, N. Y.
RECEIVED FEBRUARY 3, 1936

Theoretical Considerations Concerning the Mechanism of the Thermal Reaction between Gaseous Iodine Monochloride and Hydrogen

BY ALBERT SHERMAN AND NORMAN LI

Bonner, Gore and Yost[1] made an experimental study of the reaction

$$2\,\mathrm{ICl}\,(g) + \mathrm{H_2}\,(g) = \mathrm{I_2}\,(g) + 2\,\mathrm{HCl}\,(g)$$

and suggested tentatively the following mechanism

$$\mathrm{H_2} + \mathrm{ICl} = \mathrm{HI} + \mathrm{HCl}\ (\text{slow}) \qquad (1)$$

$$\mathrm{HI} + \mathrm{ICl} = \mathrm{HCl} + \mathrm{I_2}\ (\text{rapid}) \qquad (2)$$

They found the energy of activation for the assumed slow reaction to be 33,900 cal.

We have calculated the energies of activation for the above two reactions in order to find out whether this mechanism is reasonable. The method used in the calculations was the so-called semi-empirical one of Eyring and his co-workers[2] and will not be discussed here. The various integrals involved were evaluated by constructing Morse potential energy curves for the bonds, the coulombic energy for every bond being taken as 14% of the total energy. The constants used in constructing the Morse curves are given

Bond	r_0	w_0	D
H–H	0.74[3]	4375[3]	102.4[3]
I–Cl	2.30[3]	385[4]	49.7[8]
H–Cl	1.28[5]	2840.8[5]	101.5[6]
H–I	1.62[5]	2233[7]	69.0[6]
I–I	2.66[3]	213.7[5]	35.4[8]

The first column gives the bond, the second the equilibrium distance in Å. between the two atoms, the third gives the vibrational frequency of the lowest state in cm.$^{-1}$, and the fourth the heat of dissociation of the bond in kg. cal.

The activation energy for the reaction

$$\mathrm{H_2} + \mathrm{ICl} = \mathrm{HI} + \mathrm{HCl}$$

is calculated to be 39 kcal. as compared with the experimental value of 33.9 kcal. The agreement is fairly good, and in general is about that to be expected for such calculations.

The activation energy of the reaction

$$\mathrm{HI} + \mathrm{ICl} = \mathrm{HCl} + \mathrm{I_2}$$

was found to be 41 kcal. This energy is 2 kcal. greater than that calculated for the first reaction. Although the calculated value for the activation energy of the first reaction disagrees with the experimental value by 5 kcal., nevertheless the difference between the energies calculated for the two reactions is probably much more reliable than this, and the 2 kcal. is therefore of significance, especially the sign of the difference.

It follows that in order for the mechanism postulated by Bonner, Gore and Yost to be correct, their reaction (2) must involve some mechanism other than a bimolecular one. We suggest the following

$$\mathrm{I_2} \rightleftarrows 2\mathrm{I} \qquad (3)$$

$$\mathrm{I} + \mathrm{ICl} = \mathrm{I_2} + \mathrm{Cl} \qquad (4)$$

$$\mathrm{Cl} + \mathrm{HI} = \mathrm{HCl} + \mathrm{I} \qquad (5)$$

Equations (4) and (5) add up to equation (2), and equation (3) is the thermal dissociation of iodine. The over-all activation energy of the reaction

$$\mathrm{HI} + \mathrm{ICl} = \mathrm{HCl} + \mathrm{I_2}$$

with the above mechanism is equal approximately to the activation energy of reaction (4), calculated to be 16.3 kcal., plus one-half the heat of dissociation of iodine,[9] 17.9 kcal., or a total of 34.2 kcal.

---

[1] Bonner, Gore and Yost, THIS JOURNAL, **57**, 2723 (1935).

[2] See, for example, Van Vleck and Sherman, *Rev. Modern Phys.*, **7**, 207 (1935).

[3] R. S. Mulliken, *ibid.*, **4**, 1 (1932).

[4] W. Jevons, "Report on Band Spectra of Diatomic Molecules," Physical Society, Camb., 1932.

[5] Weizel, "Bandenspektrum," Leipzig, 1931 (Hand. der Physik—Erganzswerk bd. 1).

[6] L. Pauling, THIS JOURNAL, **54**, 3570 (1932).

[7] K. W. F. Kohlrausch, "Der Smekal-Raman Effekt," J. Springer, Berlin, 1931.

[8] W. G. Brown, *Phys. Rev.*, **37**, 1007 (1931).

[9] Van Vleck and Sherman, *Rev. Modern Phys.*, **7**, 210 (1935).

The difference between the activation energies of the reactions

$$H_2 + ICl = HI + HCl \text{ and}$$
$$HI + ICl = HCl + I_2$$

is now calculated to be 4.8 kcal., with the former reaction having the larger value. If we assume the equation

$$k = aZe^{-E/RT}$$

and consider a and Z to be the same for the two cases the ratio of the specific reaction rate constants at 220° is

$$k_2/k_1 = e^{4800/986} = 130$$

where k_1 is the specific reaction rate constant for reaction (1) and k_2 is that for (2).

We wish to point out the usefulness of activation energy calculations in just such a case as this —to aid the experimental chemist in deducing a mechanism for a reaction, a problem which primarily involves a knowledge of the difference between two energies rather than their absolute values.

Physical Chemical Laboratory
University of Wisconsin
Madison, Wisconsin
Received February 24, 1936

Catalysis by Fusions: A Reply to the Paper by Adadurow and Didenko

By E. W. R. Steacie and E. M. Elkin

In a recent paper Adadurow and Didenko[1] have criticized our work on the decomposition of methanol on solid and liquid zinc.[2] The main points in their article are as follows.

(a) They cite experiments to show that the efficiency of a silver catalyst for the oxidation of ammonia falls abruptly *in the neighborhood* of the melting point. Actually, however, it is obvious from the data that the sharp decrease in activity occurs from 40 to 130° below the melting point of silver. Their catalyst was initially porous. Their experimental description is very ambiguous, and it is difficult to decide how the experiments were made, but it appears almost certain that they were performed in order of increasing temperature. Hence as the melting point was approached sintering occurred, with an accompanying reduction in the total surface and hence in the activity. The most striking thing about their data, however, is that in every case *the efficiency of the catalyst about the melting point is greater than that immediately below it.* Their data are therefore in complete agreement with our work rather than contrary to it as they suggest.

(b) In an attempt to show that a zinc oxide layer on the surface of molten (or solid) zinc was the real catalyst in our experiments, they state "The decomposition of methyl alcohol takes place according to Bone and Davies by the equation $CH_3OH = CH_4 + O$." This is an extraordinary statement since there has never been any evidence for such a mechanism, and it is always assumed that the reaction proceeds by either dehydration or dehydrogenation.[3]

(c) On the basis of the above mechanism they conclude that a zinc oxide layer formed from the oxygen resulting from the decomposition was the active catalyst in our investigation. They go on to say "The higher the temperature the more zinc oxide is being formed, and it is plain why the work of Steacie and Elkin demonstrates here an uninterrupted growth of activity with the increase of temperature."

In our work we realized the necessity of avoiding contamination by zinc oxide. The zinc used was purified, vacuum distilled, and finally reduced with hydrogen *in situ*. Furthermore, it always maintained its metallic luster throughout a series of experiments, and no trace of zinc oxide was ever observed. Adadurow and Didenko report the oxidation of zinc on the passage of methyl alcohol vapor at 360 to 400°. No great weight can be attached to this observation, however, in the absence of any experimental details to prove the rigorous exclusion of oxygen from the reaction system.

Since each of our catalysts was used for a series of runs, it follows from Adadurow and Didenko's explanation that there should have been a progressive increase in activity from run to run. Hence an increase in activity with increasing temperature could only have occurred if experiments were always made in order of increasing temperature. Actually, however, it was shown that experiments made in order of decreasing temperature (Series VI) gave the same result. Furthermore successive runs made at the same temperature (Series V) agreed within the experimental error. Similar results were obtained in later work.[4]

---

(1) Adadurow and Didenko, This Journal, **57**, 2718 (1935).

(2) Steacie and Elkin, *Proc. Roy. Soc.* (London), **A142**, 457 (1933).

(3) Bone and Townend, "Flame and Combustion in Gases," Longmans, London, 1927; Sabatier–Reid, "Catalysis in Organic Chemistry," D. van Nostrand Co., New York, 1922; Hurd, "Pyrolysis of Carbon Compounds," Chemical Catalog Co., New York, 1929.

(4) Steacie and Elkin, *Can. J. Research*, **11**, 47 (1934).