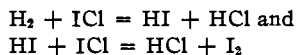


The difference between the activation energies of the reactions



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.

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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 Didenko¹ 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 im-*

mediately 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 $\text{CH}_3\text{OH} = \text{CH}_4 + \text{O}$." 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

(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).

(1) Adadurow and Didenko, *THIS JOURNAL*, **57**, 2718 (1935).

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

It also follows from the mechanism proposed by Adadurow and Didenko that the (per cent. reaction)-(time) curve for a single experiment must be autocatalytic in nature, since the reaction is assumed to be proceeding on zinc oxide formed by the decomposition of the reactant. No such effect was found, as is shown by Figure 1 of our paper.

It appears therefore that the criticisms of

Adadurow and Didenko are based partly on an incorrect interpretation of their own data, and partly on an incorrect mechanism for the decomposition of methyl alcohol. On this basis they arrive at an alternative explanation of our experiments which is not in accord with the facts.

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RECEIVED JANUARY 21, 1936

COMMUNICATIONS TO THE EDITOR

THE PHOTOLYSIS OF ACETIC ACID

Sir:

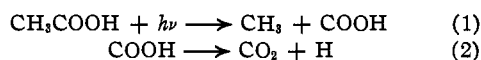
In the course of a general investigation of the mechanism of the photolysis of acetic acid I applied the method of Paneth [*Ber.*, **62B**, 1335 (1929)] to the detection of free radicals. Using a light lead mirror followed in order by a heavy lead guard mirror and a light antimony mirror, approximately simultaneous disappearance of the two light mirrors was observed.

The efficacy of the guard mirror was checked by experiments with acetone. In a particular series of experiments, it was found that a guard mirror which was ineffective in preventing the removal of an antimony mirror in an acetic acid run was, after the lapse of a day, still effective in preventing such disappearance of a fresh antimony mirror in an acetone run, even though it itself was now visibly affected. The period of the latter run was equivalent (in free radical yield) to more than twice that of the acetic acid run. When, after the latter experiment, the guard mirror was reinforced by redeposition of lead, it was found that it was still ineffective in preventing the removal of the same antimony mirror in an immediately following run with acetic acid.

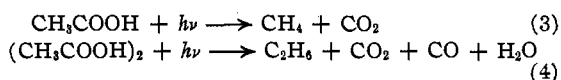
Except for the use of the guard mirror and the succeeding antimony mirror, the experiments bore a resemblance to those of Pearson [*J. Chem. Soc.*, 1718 (1934); *ibid.*, 1151 (1935)].

The effect on the lead mirrors may be attributed to the formation of free radicals, presumably methyl, and that on the antimony mirrors to the formation of atomic hydrogen in the photolysis of

acetic acid in the vapor phase according to a mechanism



Inasmuch as Farkas and Wansbrough Jones [*Z. physik. Chem.*, **B18**, 124 (1932)] offer good evidence [v. Franck and Rabinowitch, *Trans. Faraday Soc.*, **30**, 120 (1934)] for a primary formation of ultimate molecules according to the alternative mechanisms



I am led to the conclusion that, in acetic acid, decomposition may occur either from a suitable constellation of atoms by rearrangement of bonds into equally stable constellations of other molecules or from a molecule of sufficient energy content into free radicals. The implications of this conclusion are being subjected to further test.

On the basis of the results of Pearson, Robinson and Stoddard, [*Proc. Roy. Soc. (London)*, **A142**, 275 (1933)] the effect on the antimony mirror would have been unexpected since they report that the recombination of atomic hydrogen is catalyzed by a lead mirror. The results here indicate that at low concentrations of atomic hydrogen the recombination process is improbable. So far as known this is the first time that this method has been applied to the detection of hydrogen atoms in the presence of free radicals.

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RECEIVED FEBRUARY 24, 1936