If they had been, the determinations with the capillary tube and Maquenne block might have taken appreciably less time.

Table III

Speed of Determinations of Melting Points by Different Methods

Substance	I	II	III	IV	Time for the 4 detns.
Capillary tube method	118.5	121	167	91	1 hour
Maquenne block	118.5–119	120.5	166–167	91–92	4 hours[a]
Electric block	118.5	121.1	166	92.5	2 minutes
M. p. in literature	118.5	121.1	165.4	92.5	

[a] Because of difficulty in controlling the temperature of the bar.

Summary

This article describes a device for the measurement of the melting points of substances, particularly of organic substances, up to temperatures of about 300°. With the apparatus, melting points can be determined in about thirty seconds with an accuracy of about 0.25°.

Ithaca, New York

[Contribution from the Frick Chemical Laboratory, Princeton University]

A CONTRIBUTION TO THE STUDY OF CHAIN REACTIONS. (A) REMARKS ON A PAPER BY LENHER AND ROLLEFSON ON THE KINEMATICS OF PHOSGENE. (B) THE MECHANISM OF THE FORMATION AND DECOMPOSITION OF ETHYLENE IODIDE

By Hans Joachim Schumacher[1]

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Introduction

Recently a paper by Polissar[2] on the kinetics of the thermal decomposition of ethylene iodide appeared in This Journal. The decomposition was carried out in the presence of iodine in carbon tetrachloride solution. The interesting result of this careful investigation is that the velocity of the decomposition can be represented by the equation

$$-\frac{d[C_2H_4I_2]}{dt} = k[C_2H_4I_2][I_2]^{1/2}$$

This equation is, as mentioned by Polissar, similar to that of the phosgene decomposition, which is given below

$$-\frac{d[COCl_2]}{dt} = k[COCl_2][Cl_2]^{1/2}$$

Polissar, in his discussion of results, seems to have misunderstood the mechanism of the phosgene decomposition and his interpretation of the

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[1] International Research Fellow.

[2] M. J. Polissar, This Journal, 52, 956 (1930).

heat of activation in chain reactions is not very clear. These questions will be discussed in the present communication. Also, a mechanism for the formation and decomposition of ethylene iodide will be given. This mechanism, without any artificial assumptions, leads to the observed kinetic equation.

Remarks on the Phosgene Reaction.—The kinetics and photochemistry of phosgene have been intensively investigated by Bodenstein and co-workers.[3] All this previous work together with recent unpublished investigations will be thoroughly discussed in a forthcoming publication.[4] In this paper a theory will be given which enables one to represent quantitatively the thermal and photo-kinetics of this complicated reaction. Also, a mechanism will be given by which the carbon dioxide formation (sensitized by chlorine) can be interpreted. This is closely related to the phosgene reaction.

The basis of the mechanism of the phosgene reaction is that which has been given by Bodenstein, Lenher and Wagner.[3]

$$\mathrm{Cl_2} + h\nu \longrightarrow \mathrm{Cl} + \mathrm{Cl} \qquad (1)$$

$$\left.\begin{aligned} \mathrm{Cl} + \mathrm{CO} &\longrightarrow \mathrm{COCl} \\ \mathrm{COC} &\longrightarrow \mathrm{CO} + \mathrm{Cl} \end{aligned}\right\} \text{Equilibrium} \qquad \begin{aligned}(2)\\(3)\end{aligned}$$

$$\mathrm{CO} + \mathrm{Cl} + \mathrm{Cl_2} \longrightarrow \mathrm{COCl_2} + \mathrm{C} \qquad (4)$$

$$\mathrm{Cl} + \mathrm{COCl} \longrightarrow \mathrm{CO} + \mathrm{Cl_2} \qquad (5)$$

This mechanism has recently been criticized by Lenher and Rollefson,[5] who substitute another mechanism. In the following it will be shown that their objections are not substantiated and that their proposed mechanism is highly improbable.

(I) In the mechanism proposed by Bodenstein, Lenher and Wagner Reactions 2 and 3 proceed at such a velocity that the COCl concentration is always equal to its equilibrium concentration. Equation 4 has only a formal meaning. It can, as was pointed out by Bodenstein, Lenher and Wagner,[6] be replaced by the reaction

$$\mathrm{COCl} + \mathrm{Cl_2} \longrightarrow \mathrm{COCl_2} + \mathrm{Cl}$$

assuming, of course, that the COCl equilibrium is not disturbed. Evidently this has been overlooked by Lenher and Rollefson, who say that they cannot understand why COCl should react with oxygen and not with chlorine. This is not required at all. In order to explain the experimental fact that the phosgene reaction is strongly inhibited by small amounts of oxygen, it has to be assumed that the COCl reacts much faster with oxygen than with chlorine. There does not seem to be any difficulty in

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[3] (a) M. Bodenstein and Plaut, *Z. physik. Chem.*, **110**, 399 (1924); (b) M. Bodenstein, *ibid.*, **130**, 422 (1927); (c) H. J. Schumacher, *ibid.*, **129**, 241 (1927); (d) M. Bodenstein and Onoda, *ibid.*, **131**, 153 (1927); (e) M. Bodenstein, S. Lenher and C. Wagner, *ibid.*, **3B**, 459 (1929).

[4] M. Bodenstein, H. J. Schumacher and G. Stieger, *ibid.*, in press (1930).

[5] Lenher and Rollefson, This Journal, **52**, 500 (1930).

[6] Bodenstein, Lenher and Wagner, Ref. 3, p. 470.

this conception and Lenher and Rollefson have to make the same assumption in their own scheme in order to account for the inhibiting influence of oxygen.

(II) Lenher and Rollefson see difficulty in that the COCl always has to be at its equilibrium concentration. In reference to this the following can be said. The heat of formation of COCl from CO and Cl can be estimated to be about 5 cal. Indeed the formation of COCl can only occur in a three-body collision, which means that the quasi-molecule COCl has, in order to be stabilized, to collide with another molecule within its life of about 10^{-13} sec.[7] But except in the case of very low pressures three-body collisions are so frequent that the velocity of formation is sufficient. In consequence of the small heat of formation the COCl is decomposed fast enough. Therefore, there is no reason to throw out the existence of the COCl equilibrium.

(III) The third point in the objections of Lenher and Rollefson, namely, that reactions of Type 4 take place very seldom, was partly settled under (I). There we have shown that the above Reaction 4 can be substituted by the reaction

$$COCl + Cl_2 \longrightarrow COCl_2 + Cl$$

It is however to be emphasized that reactions of Type 4 are quite possible and, in fact, the probability of such a reaction can be great,[8] although of course, Reaction 4 has only a formal meaning, as has been mentioned before.

The above indicates that the objections of Lenher and Rollefson are not valid. These authors propose the mechanism

$$\begin{aligned} Cl_2 + h\nu &\longrightarrow Cl + Cl && (1)\\ CO + Cl + X &\longrightarrow COCl + X && (2)\\ COCl + Cl_2 &\longrightarrow COCl_2 + Cl && (3)\\ COCl + Cl &\longrightarrow CO + Cl_2 && (4) \end{aligned}$$

According to this the COCl is not present in its equilibrium concentration. In order to obtain the right equation for the reaction velocity it has to be postulated that COCl can be formed only if it is stabilized by a collision with a chlorine molecule. This means that X in Equation 2 is equal to Cl_2. All other gases are not supposed to have any influence on the process.

To this it can be said that the law for the reaction velocity for the phosgene formation is still valid if Cl_2 compared with other gases (CO, $COCl_2$, CO_2) is present in small concentration (1 to 50 and less). In order to exclude the influence of these gases on Reaction 2 it has to be assumed that chlorine is several hundred times as efficient as these gases. It has

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[7] Herzfeld, *Ann. Physik*, **59**, 635 (1919).

[8] Lenher and Rollefson believe that these reactions are improbable and make reference to a paper by Frenkel and Semenoff [*Z. Physik*, **48**, 216 (1928)]. The probability given by these authors, as has been shown by Jost [*Z. physik. Chem.*, **3B**, 126 (1929)] is too small by a factor of about 10^5.

to be emphasized that such an assumption is contradictory to all known experimental facts. Lenher and Rollefson cite as proof of their theory the specific effect of different gases on the quenching of fluorescence radiation. Apart from the fact that CO and CO_2 quench the fluorescence generally very well, it must be pointed out that the three-body collision is quite a different process. As is well known, in a three-body collision the third molecule has to take up only that part of the energy of the quasi-molecule which separates it from a stable state. This can be a very small amount and normally is of the order of magnitude of the mean kinetic energy of molecules. Only monatomic gases are usually relatively inefficient.[9] Polyatomic gases are usually in their efficiency as third bodies only different by a factor smaller than three.[10] It does not seem probable that chlorine should be several hundred times as efficient as the other polyatomic gases, so it must be said that the mechanism proposed by Lenher and Rollefson is rather improbable.

Discussion of Polissar's Interpretation of the Heat of Activation of the Phosgene Reaction.—The heat of activation of a bimolecular reaction, as determined from the temperature coefficient, is the minimum energy in excess of the average energy, which any two molecules must have in order to react upon collision.[11] The question of whether the activation energy is to be considered as internal or as kinetic energy will not be discussed here, there being already considerable literature on this point.[12]

In the case of chain reactions, of course, the value of Q, the heat of activation determined from the temperature coefficient, loses its simple physical significance. In such reactions the value of Q is made of the Q' of the reactions forming the different stages of the total reaction. Bodenstein and his co-workers[13] have published examples of the method of calculation in such cases.

Now the thermal decomposition of phosgene is a typical chain reaction,[14] the heat of activation of the various stages having been calculated by Bodenstein and Plaut. Polissar does not consider this mechanism. His value of 24 Cal. for Q'' corresponds to the reaction

$$COCl_2 + Cl \longrightarrow COCl + Cl_2$$

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[9] W. Jost, *Z. physik. Chem.*, **3B**, 95 (1929).

[10] H. J. Schumacher, THIS JOURNAL, **52**, 2377 (1930).

[11] J. A. Christiansen, *Proc. Cambridge Soc.*, [XXIII] **4**, 438 (1926).

[12] Kallman and London, *Z. physik. Chem.*, **2B**, 207 (1929); Fowler, "Statistical Mechanics," **1929**, p. 462; H. J. Schumacher and G. Sprenger, *Z. physik. Chem.*, **6B**, 446 (1930); Arne Olander, *ibid.*, **7**, 311 (1930); H. J. Schumacher, *ibid.*, **8B**, 218 (1930); L. S. Kassel, *Phys. Rev.*, **35**, 261 (1930); D. S. Villars, *ibid.*, **34**, 1063 (1929); THIS JOURNAL, **52**, 1733 (1930).

[13] M. Bodenstein, E. Padelt and H. J. Schumacher, *Z. physik. Chem.*, 5B, 209 (1929); H. J. Schumacher and G. Sprenger, *ibid.*, **2B**, 267 (1929).

[14] J. A. Christiansen, "Reaktionskinetiske Studier," Priors Hofboghandel, Kopenhagen; M. Bodenstein and Plaut, *Z. physik. Chem.*, **110**, 400 (1924).

The reaction between Q'' and the heat of dissociation of phosgene is such that the sum of Q'' and the dissociation energy of COCl must be equal to the dissociation energy of $COCl_2$. It is assumed that reaction takes place in every collision, when the reaction is exothermic. Only then the relation is correct. Q_{COCl} has a value of about 5 Cal.[3e]

The ease with which the second Cl atom is split off from $COCl_2$ is explained by the fact that when the Cl atom is removed from COCl the carbon atom passes back from the (^5S) to the (^3P) state.[15] Simultaneously, energy is liberated corresponding to the energy difference of these two states. This energy is just of the right order of magnitude.[15b]

The Mechanism of the Decomposition of Ethylene Iodine Catalyzed by Iodine.—As Polissar found, the decomposition of $C_2H_4I_2$ catalyzed by I_2 takes place according to the equation

$$-\frac{d[C_2H_4I_2]}{dt} = k[C_2H_4I_2]\ [I_2]^{1/2}$$

Consequently, the equation for the synthesis is

$$+\frac{d[C_2H_4I_2]}{dt} = k'[C_2H_4][I_2]^{3/2}$$

The following scheme is given by Polissar

(a) Synthesis

$$\begin{array}{rclr} I_2 & \rightleftarrows & I + I & (1) \\ I + I_2 + C_2H_4 & \longrightarrow & C_2H_4I_2 + I & (2) \end{array}$$

(b) Decomposition

$$\begin{array}{rclr} I_2 & \longrightarrow & I + I & (1) \\ I + C_2H_4I_2 & \longrightarrow & C_2H_4 + I + I_2 & (2) \end{array}$$

Reaction 2 has evidently only formal but no chemical significance. By analogy with the mechanism of the phosgene reaction, the following mechanism is suggested

(a) Synthesis

$$\begin{array}{lr} I_2 \rightleftarrows I + I & (1a) \\ \left.\begin{array}{rcl} I + C_2H_4 & \longrightarrow & C_2H_4I \\ C_2H_4I & \longrightarrow & C_2H_4 + I \end{array}\right\} \text{equilibrium} & \begin{array}{r}(2a)\\(3a)\end{array} \\ C\ H_4I + I_2 \longrightarrow C_2H_4I_2 + I & (4a) \end{array}$$

(b) Decomposition

$$\begin{array}{lr} I_2 \rightleftarrows I + I & (1b) \\ C_2H_4I_2 + I \longrightarrow C_2H_4I + I_2 & (2b) \\ \left.\begin{array}{rcl} C\ H_4I & \longrightarrow & C_2H_4 + I \\ C_2H_4 + I & \longrightarrow & C_2H_4I \end{array}\right\} \text{equilibrium} & \begin{array}{r}(3b)\\(4b)\end{array} \end{array}$$

The rate of the synthesis is determined by Reaction 4a and that of the decomposition by 2b. Both iodine atoms and C_2H_4I molecules should be present throughout in their equilibrium concentrations. If such is the case, the expression for the synthesis becomes

$$+\frac{d[C_2H_4I_2]}{dt} = k_4 \times K_{C_2H_4I} \times K_{I_2}{}^{1/2} \times [C_2H_4][I_2]^{1/2} \qquad (I)$$

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[15] (a) F. London, *Z. Physik*, **46**, 455 (1928); (b) R. Mecke, *Z. physik. Chem.*, **7B**, 108 (1930).

where $K_{C_2H_4I} = k_2/k_3$ and K_{I_2} are the equilibrium constants of the corresponding reactions. For the decomposition we get

$$-\frac{d[C_2H_4I_2]}{dt} = k_2K_{I_2}^{1/2}[C_2H_4I_2][I_2]^{1/2} \tag{II}$$

These correspond with the equations found by experiment. From the form of the equation it is seen that iodine atoms can recombine only according to Reaction 1 but not according to the equation $C_2H_4I + I \longrightarrow C_2H_4 + I_2$. That is to say, the concentration of C_2H_4I must be very small. This will be the case when the heat of the reaction $C_2H_4 + I \longrightarrow C_2H_4I$ is very low.

The reaction $I + I \longrightarrow I_2$ depends on three-body collisions. In solution it should be practically independent of pressure, or at least the effect will be small.

Polissar determined experimentally the heat of decomposition of ethylene iodide into ethylene and iodine, the velocity constants of the decomposition and their dependence on temperature. Bodenstein[16] has already measured the equilibrium between iodine and iodine atoms, and sufficient data are therefore available for the calculations of heat of activation of the component reactions in the decomposition of ethylene iodide.

According to Polissar, for $T = 425°$ the velocity constant $k = 710 \times 10^{-4}$; for $T = 415°$, $k = 278 \times 10^{-4}$. From these figures the apparent heat of activation at this temperature is 32.800 cal. = Q. It follows from Equation II that $k = k_2\sqrt{K}$. Consequently $32.800 = Q'' + \frac{1}{2}Q'$, when Q'' is the heat of activation of Reaction 2b and Q' is the heat of dissociation of iodine at 420°. According to Bodenstein and Stark[16]

$$Q' = 35.400 + 3.5T - 0.0019T^2$$

i. e., $Q'_{420} = 36.600$ Cal., and the value of Q'' so obtained

$$Q'' = 32.800 - 18.300 = 14.500 \text{ Cal.}$$

Since Polissar's values of the velocity constants are not very exact, the same calculations have been repeated for 405° and 395°, and the average value of Q'' taken.

$$k_{405°} = 119 \times 10^{-4};\quad k_{395°} = 47.2 \times 10^{-4}$$

The corresponding values are

$$Q_{410°} = 28.300 \text{ Cal. and } Q''_{410°} = 28.300 - 18.250 = 10.050 \text{ Cal.}$$
$$Q_{400°} = 28.00 \text{ Cal. and } Q''_{400°} = 28.000 - 18.250 = 9.750 \text{ Cal.}$$

Taking the average and neglecting the dependence of Q'' on temperature, the value of Q'' for the reaction

$$C_2H_4I_2 + I \longrightarrow C_2H_4I + I_2$$

comes out to be

$$Q''_{410°} = 11.500 \text{ Cal.}$$

This value of Q'' is correct to about 2 cal.

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[16] M. Bodenstein and Stark, *Z. Elektrochem.*, **16**, 961 (1910).

According to a general principle, due to Trautz, the heat of reaction may be expressed as the difference of the heats of activation of the forward and the reverse reaction. In the case of exchange reactions, in which atoms or radicals take part, reaction takes place in every collision, if the process is exothermic. Some exceptions[17] to this rule, given by Polanyi,[18] have recently been found, but it can nevertheless be taken as generally valid. Assuming it in the case of the reaction between $C_2H_4I_2$ + I and of the reverse reaction $C_2H_4I + I_2$, Q'' will then represent the heat of this reaction.

$$I_2 + C_2H_4I \longrightarrow C_2H_4I_2 + I + 11.500 \text{ Cal.}$$

As is evident by comparing Equations I and II, $Q_{C_2H_4I}$ will have the low value of 0.200 Cal., since Polissar gave the heat of the total reaction as 11.300 Cal. The value of $Q_{C_2H_4I}$ is also correct only to a few calories. A low value of Q is, however, to be expected. Having obtained this, the heat of activation has been determined for every reaction which takes part in the formation and decomposition of $C_2H_4I_2$ in the presence of iodine.

Calculations of Strength of Binding from Thermal Data.—From the thermal data we can calculate the value of the C—I linkage in $C_2H_4I_2$ and of the difference in energy between the carbon double bond in C_2H_4 and the C—C bond in $C_2H_4I_2$. In the dissociation of $C_2H_4I_2$ into C_2H_4 and I_2, two C—I linkages are broken, one C=C linkage and one iodine molecule being produced. This is expressed by the equation

$$2\,(\text{C—I}) = \text{C=C} + I_2 + Q$$

where Q = 11.300 Cal., I_2 = 36.500 Cal. is the heat of formation of I_2 at the temperature in question and C=C is the energy difference between the single and the double carbon linkage.

$$2\text{C—I} = \text{C=C} + 47.8 \text{ Cal.} \qquad \text{(A)}$$

We have calculated

$$C_2H_4I \longrightarrow C_2H_4 + I - 0.2 \text{ Cal., } i.\,e.,$$
$$\text{C—I} = \text{C=C} - 0.2 \text{ Cal.} \qquad \text{(B)}$$

and from A–B

$$\text{C—I} = 48 \text{ Cal.}$$

That is, the value of the linkage between carbon and iodine is 48 Cal., which is higher than the value determined from the thermal data. Grimm[19] gave an average value for the C—I linkage of 44 Cal. Bates and Andrews[20] give 40 Cal., but in the value we obtained, a part of the excitation energy of a (^3P) to a (^5S) carbon atom is included.

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[17] G. B. Kistiakowsky, This Journal, **52**, 1868 (1930); H. J. Schumacher, *ibid.*, **52**, 2377 (1930).

[18] Beutler and Polanyi, *Z. physik. Chem.*, 1B, 3 (1928); Bogdandy and Polanyi, *ibid.*, 1B, 21 (1928); Polanyi and Schay, *ibid.*, 1B, 30 (1928).

[19] Grimm, "Handbuch der Physik," Vol. XXIV, p. 536.

[20] Bates and Andrews, *Proc. Nat. Acad. Sci.*, 14, 124 (1928).

For the energy difference between C=C and C—C the value 48.2 Cal. is obtained, whereas Grimm gave an average value of 54.

It is now easily understood why the second iodine atom splits off so readily from $C_2H_4I_2$, for this process is coupled with the liberation of energy accompanying the formation of the C=C bond.

In the case of phosgene it was the transition of the C atom from the (^5S) to the (^3P) state which made the Cl atom readily removable. The energy difference of these two states, as can be calculated from kinetic data,[3e] has the value of 74 Cal., in agreement with the value of 60–100 Cal. given by Mecke.[15b]

The author wishes to express his thanks to Dr. H. J. Emeléus and Dr. G. I. Lavin of this Laboratory for translating the paper into English.

Summary

1. An article of Lenher and Rollefson on the mechanism of the phosgene reaction is discussed.

2. A mechanism of the reaction between iodine and ethylene iodide and iodine and ethylene is given, and the heats of activation of the component reactions are calculated.

3. From the thermal and kinetic data the energy difference between the (^5S) and the (^3P) state of the carbon atom is found to be 74 Cal. Both for the C—I linkage in ethylene iodide and for the energy difference between C—C and C=C a value of about 48 Cal. is obtained.

PRINCETON, NEW JERSEY

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

PRECISION ACTINOMETRY WITH URANYL OXALATE

BY WESLEY GLICK LEIGHTON AND GEORGE SHANNON FORBES

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For actinometry, uranyl sulfate with excess of oxalic acid has marked advantages, such as absence of dark reaction, great width of absorption band, zero order light reaction, a temperature coefficient of approximately unity, small effect of added electrolytes and finally the simplicity of the permanganate method of analysis. Boll[1] reported 50 molecules transformed per quantum at 254 mμ; Büchi[2] 1.07 between 400 and 470 mμ; Bowen and Watts[3] 1.0 at mean wave length 313 mμ; and Anderson and Robinson[4] 0.04 between 200 and 410 mμ. The system would doubtless be more useful to photochemists if the quantum yield were better known.

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[1] Boll, *Compt. rend.*, **156**, 1891 (1913).

[2] Büchi, *Z. physik. Chem.*, **111**, 269 (1924).

[3] Bowen and Watts, *J. Chem. Soc.*, 1607 (1926).

[4] Anderson and Robinson, THIS JOURNAL, **47**, 718 (1925).