NOTES

The Kinetics of the Thermal Decomposition of Gaseous Methyl Iodide

By E. W. R. Steacie and R. D. McDonald

In a recent paper[1] Ogg has reported an investigation of the reactions of gaseous alkyl iodides with hydrogen iodide. From the results obtained he concludes that a part of the process can be attributed to a preliminary unimolecular decomposition of the alkyl iodides. In this way he arrives indirectly at the expression

$$K_\infty = 3.93 \times 10^{12} e^{-43,000/RT}\ \text{sec.}^{-1}$$

for the velocity constant of the methyl iodide decomposition. Actually, however, methyl iodide is more stable than would be expected on this basis, and he therefore concludes that the reverse reaction is also taking place, *viz.*

$$\begin{aligned} CH_3I &\longrightarrow CH_3^- + I && (1)\\ CH_3^- + I &\longrightarrow CH_3I && (2) \end{aligned}$$

the other possible reactions of the methyl radicals

$$\begin{aligned} 2CH_3 &\longrightarrow C_2H_6 && (3)\\ \left\{\begin{aligned} 2CH_3 &\longrightarrow CH_2^- + CH_4\\ 2CH_2 &\longrightarrow C_2H_4 \end{aligned}\right. & && (4)\\ CH_3 + CH_3I &\longrightarrow C_2H_6 + I && (5) \end{aligned}$$

being unimportant compared with (2).

Shortly before the appearance of Ogg's paper we had submitted a short note on a direct investigation of the methyl iodide decomposition.[2] This report was qualitative only since side reactions, etc., were too complex to make a detailed kinetic investigation worth while. It is, however, possible to make a rough comparison of the rate with that inferred by Ogg.

From our results T_{50} is of the order of magnitude of 100 seconds at 510°. This is a lower limit since some heterogeneous reaction is also present. Ogg's equation indicates a value of about 0.2 sec. at this temperature. Hence the rate at 510° is $^1/_{500}$ or less of the rate calculated. In view of the low strength of the carbon–iodine linkage (about 40,000 cal.), the stability of methyl iodide seems best explained on the basis of Ogg's scheme (reactions (1) and (2)). The actual decomposition at high temperatures cannot follow reaction (3) or (5), since these would lead to the production of ethane, without condensation or carbon deposition. The large amount of condensation and carbon deposition are in accord with expectations if reaction (4) represents the main course of the decomposition at high temperatures.

It appears, therefore, that qualitative results on the direct decomposition of methyl iodide are in complete accord with Ogg's inferences.

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[1] Ogg, This Journal, **56**, 526 (1934).

[2] *Can. J. Research*, **10**, 591 (1934).

Solution of the Conductance Equation

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The conductance of incompletely dissociated binary electrolytes as a function of concentration obeys the equation[1,2]

$$\Lambda = \gamma(\Lambda_0 - \alpha\sqrt{c\gamma}) \qquad (1)$$

exactly up to concentrations at which specific ionic interactions of higher order than pairwise become appreciable. (This concentration is in order of magnitude $3.2 \times 10^{-7} D^3$ at 25°, where D is the dielectric constant of the solvent.[3]) At present, the solution of (1), given α, c, Λ and Λ_0, for γ, the fraction of salt existing as free ions, involves a very tedious series of successive approximations.

If we introduce a new variable z, defined as follows

$$z = \alpha\Lambda_0^{-3/2}\sqrt{c\Lambda} = \alpha\Lambda_0^{-3/2}\sqrt{1000\,\kappa} \qquad (2)$$

where α = the Onsager coefficient, Λ_0 = limiting conductance, c = concentration in equivalents per liter, Λ = equivalent conductance and κ = specific conductance, equation (1) may be written

$$\gamma = \Lambda/\Lambda_0 F(z) \qquad (3)$$

where $F(z)$ is the continued fraction

$$F(z) = 1 - z(1 - z(1 - z(1 - \ldots)^{-1/2})^{-1/2})^{-1/2} \qquad (4)$$

Values of this function for round values of z from $z = 0.000$ to $z = 0.209$ are given in Table I, at intervals $\Delta z = 0.001$. For example, $F(0.1044) = 0.88928$.

In order to solve (1) for γ, a value of z is computed, the corresponding value of $F(z)$ is interpolated from the table, and γ is simply obtained by division of the conductance ratio Λ/Λ_0' by F.

In order to obtain Λ_0 and K from conductance data, a free-hand extrapolation of a Λ–$\sqrt{c}$ plot is made, in order to obtain a tentative value Λ_0'

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[1] Fuoss and Kraus, This Journal, **55**, 476 (1933).

[2] Shedlovsky and Uhlig, *J. Gen. Physiol.*, **17**, 549 (1934).

[3] Fuoss, unpublished calculations.