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.*

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

the other possible reactions of the methyl radicals

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

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.

Physical Chemistry Laboratory
McGill University
Montreal, Canada

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

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

Solution of the Conductance Equation

By Raymond M. Fuoss

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 Δz = 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.

TABLE I

INTERPOLATION TABLE FOR $F(z)$

z	0.000	0.001	0.002	0.003	0.004	0.005	0.006	0.007	0.008	0.009	Diff.
0.000	1.00000	0.99900	0.99800	0.99700	0.99599	0.99499	0.99398	0.99297	0.99197	0.99096	100
.010	.98995	.98894	.98793	.98691	.98590	.98489	.98387	.98285	.98184	.98082	102
.020	.97980	.97877	.97775	.97672	.97570	.97468	.97365	.97263	.97160	.97056	103
.030	.96953	.96850	.96747	.96644	.96540	.96437	.96333	.96229	.96125	.96021	104
.040	.95916	.95812	.95708	.95603	.95498	.95394	.95289	.95184	.95078	.94973	105
.050	.94867	.94762	.94656	.94550	.94444	.94338	.94232	.94126	.94019	.93912	106
.060	.93805	.93698	.93591	.93483	.93376	.93268	.93161	.93053	.92946	.92838	107
.070	.92731	.92623	.92514	.92406	.92297	.92188	.92079	.91970	.91861	.91752	109
.080	.91643	.91534	.91424	.91314	.91204	.91094	.90984	.90873	.90763	.90653	110
.090	.90542	.90431	.90319	.90208	.90096	.89985	.89873	.89761	.89649	.89537	112
.100	.89425	.89312	.89199	.89086	.88973	.88860	.88747	.88634	.88521	.88408	113
.110	.88294	.88180	.88065	.87950	.87835	.87720	.87605	.87490	.87375	.87260	115
.120	.87145	.87029	.86913	.86797	.86681	.86565	.86448	.86331	.86214	.86097	117
.130	.85980	.85862	.85744	.85626	.85508	.85390	.85272	.85154	.85035	.84916	118
.140	.84797	.84677	.84557	.84437	.84317	.84197	.84077	.83957	.83836	.83715	120
.150	.83594	.83472	.83350	.83228	.83106	.82984	.82862	.82740	.82617	.82494	122
.160	.82371	.82247	.82123	.81999	.81875	.81751	.81626	.81501	.81376	.81251	125
.170	.81126	.81000	.80874	.80748	.80621	.80494	.80367	.80240	.80113	.79985	127
.180	.79857	.79728	.79599	.79470	.79341	.79212	.79083	.78954	.78824	.78694	129
.190	.78564	.78433	.78302	.78171	.78039	.77907	.77775	.77643	.77510	.77377	132
.200	.77244	.77110	.76976	.76841	.76706	.76571	.76436	.76301	.76166	.76031	135

for the limiting conductance. With this tentative value, γ is calculated from Λ (observed) by (3) and then the activity by means of the equation

$$-\log_{10} f^2 = 2\beta\sqrt{c\gamma} \tag{5}$$

(The term in κa is omitted here, because it arises from ions in contact, and these are counted as associated pairs.) Finally F/Λ is plotted against $c\Lambda f^2/F$. For concentrations less than 3×10^{-7} D^3, a straight line is obtained, with intercept $1/\Lambda_0$ and slope $1/K\Lambda_0^2$. This method, which is simply a correction for long range interionic forces of the Ostwald dilution law used by Kraus and Bray,[4] is very much less laborious than the previous method[1] of successive approximations.

[4] Kraus and Bray, THIS JOURNAL, **35**, 1315 (1913).

CHEMICAL LABORATORY OF
BROWN UNIVERSITY
PROVIDENCE, R. I.

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The Decomposition Voltage of Grignard Reagents in Ether Solution

BY W. V. EVANS, F. H. LEE AND C. H. LEE

The Grignard reagent has been electrolyzed,[1,2] the hydrocarbons appearing as anodic products have been isolated quantitatively and identified and the faraday equivalent of the cathodic product, magnesium, determined.

By assuming that the discharge potential of the magnesium is constant it should be possible to determine the discharge potentials of various organic groups in Grignard solutions of a definite composition.

Experimental

Preparation of Solutions.—Dry ether, purified Eastman alkyl and aryl bromides and special magnesium were used as raw materials. The magnesium for the preparation of the Grignard solutions was always in excess of the amount necessary for the reaction RX + Mg = RMgX. In each preparation the reaction mixture was heated over a water-bath after reaction. A portion of the solution was analyzed by Gilman's titration method and the remainder diluted to approximately molar concentration and then transferred to an enclosed conductivity cell for decomposition measurement. The solutions during preparation and transfer were kept in contact with dry hydrogen.

Measurement of the Decomposition Voltage.—The apparatus used for measuring the de-

[1] Kondyrew and Manojew, *Ber.*, **58**, 464 (1925).

[2] Evans and Lee, THIS JOURNAL, **56**, 654 (1934).