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

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

(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).

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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-

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

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

composition voltage is shown in Fig. 1. The cell C was kept at 22°. Galvanometer G, shunted in each experiment with a suitable resistance R, was used to measure the current passing through the cell. A low voltage was applied at the beginning and after a constant current was obtained the voltage gradually was increased usually to about five volts, and the corresponding galvanometer readings taken in a similar manner. The galvanometer readings were then plotted against the corresponding voltages. The voltage where the curve showed a distinct break was taken as the decomposition voltage. In most cases two results were obtained showing the possibility of checking such results. Check measurements were made with the current reversed. Table I shows the values obtained.

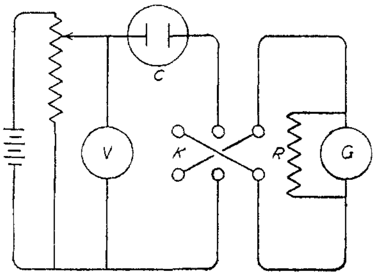

Fig. 1.

Table I

Reagent	Concentration	Decomposition voltage	Average
C_6H_5MgBr	1.02 1.04	2.21 2.13	2.17
CH_3MgBr	1.09	1.94	1.94
C_3H_7MgBr	1.01 0.92	1.41 1.43	1.42
C_4H_9MgBr	1.06 1.00	1.31 1.33	1.32
C_2H_5MgBr	1.56 1.03	1.27 1.29	1.28
$C_2H_5(CH_3)CHMgBr$	1.03 1.00	1.23 1.25	1.24
$(CH_3)_2CHMgBr$	0.95 0.98	1.08 1.06	1.07
$(CH_3)_3CMgBr$	.81 .86	0.91 1.03	0.97
$CH_2{=}CHCH_2MgBr$	.87 1.13	.83 0.89	.86

Graphs for two typical results, ethylmagnesium bromide and methylmagnesium bromide, are shown in Fig. 2.

Discussion

The data indicate that the decomposition voltages of the Grignard reagents tested do vary and range from 2.17 to 0.86 volts. If we assume the discharge potential of the magnesium constant in these solutions we then have a set of numbers that show us the relative discharge potential of each alkyl and aryl anion constituting the reagents. We note that the phenyl anion has a higher discharge potential than the saturated alkyl radicals while allyl has the lowest discharge potential. Among isomeric radicals the order is primary, secondary and tertiary in descending order.

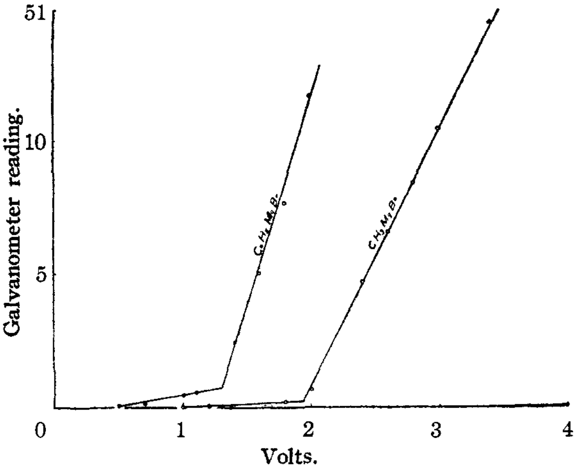

Fig. 2.

When we replace hydrogen atoms by methyl groups in a methyl radical the discharge potential of the substituted methyl radicals is gradually lowered since the discharge potential of methyl, ethyl, isopropyl and tertiary butyl radicals are, respectively, 1.94, 1.28, 1.07 and 0.97 volts.

Summary

1. The decomposition potentials of molar solutions of phenylmagnesium bromide, methylmagnesium bromide, ethylmagnesium bromide, *n*-, and *i*-propylmagnesium bromides, *n*, *s*, and *t*-butylmagnesium bromides and allylmagnesium bromide have been determined at 22°.

2. The effect on discharge potential of substituting a methyl group for hydrogen in a methyl radical has been presented. Comparison has been made as to the discharge potentials of isomeric alkyls.

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