thermochemical data on energies of formation. The energy difference between rotational isomers has been calculated for the structural element C_2-C_2 (n-butane) as 0.66 kcal/mole, the experimental value for n-butane being 0.77 kcal/mole.

5. A quantum-mechanical interpretation of the equations has been given in terms of the localised-valency-pair method based on the Slater formula and its generalisation in Mamotenko's formula, and it has been shown that the constants occurring in Eqn. (5) can be expressed in terms of appropriate quantum-mechanical integrals.

6. The quantum-mechanical method of deriving the equations can be employed for molecules of any type. The equations obtained (when the immediate environment only of a bond is taken into account) will always be analogous to those that follow from the types and forms of chemical bonds which have been previously introduced by one of the authors.

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Lomonosov State University, Moscow

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THEORY OF THE ELECTRODEPOSITION OF METALS FROM COMPLEX SOLUTIONS

E. A. Ukshe

The present paper reports measurements of cathodic polarisation in the electrodeposition of metals.

EXPERIMENTAL

Copper Pyrophosphate Electrolytes

A copper pyrophosphate electrolyte is an extremely convenient medium for studying cathodic processes, and is also valuable in plating. The cathodic polarisation in the electrodeposition of copper from pyrophosphate electrolytes has already been studied by Gorbachev and Izmailov[1] and by ourselves[2], but these studies were not completely satisfactory; either the deviation of the current yield of copper from 100% was overlooked, or too narrow a range of compositions and current densities was studied. We have therefore measured the cathodic polarisation in solutions of total composition 0.04 M $CuSO_4$ + 0.09–0.19 M $Na_4P_2O_7$ at current densities from 0.4 to 3.0 mA/cm².

The measurements were made in a 250 ml cell in an atmosphere of air or hydrogen. The cathode and anode were platinum, copper-plated in a sulphuric acid electrolyte, the free end of the cathode being fused into glass. The current yield was determined in three separate cells with removable cathodes, which were filled with the same solution, connected in series, and kept at 25° ± 0.5°. The solutions were not stirred.

A calibrated millivoltmeter with valve amplifier LLPU-1 was used to determine the cathode potentials; 1 scale division of the millivoltmeter corresponded to 1 mV. The probable error in the potential measured against a saturated calomel comparison electrode was determined from the assumed normal distribution given by the equation[3]

$$\sigma_\varphi = 0.675\sqrt{\frac{\Sigma y_i}{n}},$$

where n is the total number of measurements, assumed to be of equal accuracy (in all the experiments $n = 3$), and y_i is the deviation of each measurement from the arithmetic mean. The probable deviation in the potential was 2–3 mV in our case.

The current was measured with a milliammeter with 0.05 mA scale divisions. Since the current yield was determined with an error of 2–3%, the probable error in determining the electrodeposition current is not more than 0.03 mA/cm². Thus the relative accuracy in the measured potential was considerably greater than in the electrodeposition current. This is due to the deviation of the current yield from unity. The results of the measurements are collected in Table 1.

Using the instability constants of the pyrophosphate complexes of copper for a solution of 0.04 M $CuSO_4$ + 0.09 M $Na_4P_2O_7$, we have approximately

$$c_{Cu^{++}} \cong 10^{-8.1}\ M; \quad c_{[Cu(P_2O_7)]^{2-}} \cong 10^{-5}\ M; \quad c_{[Cu(P_2O_7)_2]^{6-}} \cong 4 \cdot 10^{-2}\ M,$$

TABLE 1. Cathodic polarisation in the electrodeposition of copper from pyrophosphate electrolytes.

i, mA/cm²	$c_{Na_4P_2O_7} = 0.09$ M, $\varphi_1 = 0.105$ V			$c_{Na_4P_2O_7} = 0.11$ M, $\varphi_2 = 0.065$ V			$c_{Na_4P_2O_7} = 0.13$ M, $\varphi_3 = 0.045$ V			$c_{Na_4P_2O_7} = 0.15$ M, $\varphi_4 = 0.020$ V			$c_{Na_4P_2O_7} = 0.17$ M, $\varphi_5 = 0.008$ V			$c_{Na_4P_2O_7} = 0.19$ M, $\varphi_6 = 0.002$ V		
	A	i	Δφ	A	i	Δφ	A	i	Δφ	A	i	Δφ	A	i	Δφ	A	i	Δφ
3.0	0.55	0.65	1.157	0.543	1.63	1.107	0.540	1.62	1.090	0.545	1.63	1.087	0.545	1.63	1.066	0.54	1.62	1.077
2.8	0.58	1.62	1.102	0.58	1.62	1.060	0.575	1.61	1.039	0.58	1.62	1.027	0.58	1.62	1.045	0.57	1.60	1.018
2.6	0.62	1.61	1.064	0.62	1.61	1.020	0.615	1.60	1.014	0.62	1.61	0.997	0.62	1.61	1.000	0.61	1.59	0.977
2.4	0.67	1.60	1.054	0.67	1.60	1.000	0.670	1.598	1.000	0.66	1.58	0.942	0.66	1.58	0.930	0.65	1.56	0.930
2.2	0.72	1.58	0.977	0.72	1.58	0.962	0.700	1.54	0.934	0.70	1.54	0.905	0.70	1.54	0.897	0.70	1.54	0.907
2.0	0.76	1.52	0.937	0.77	1.54	0.900	0.730	1.46	0.870	0.73	1.46	0.842	0.75	1.50	0.855	0.75	1.50	0.877
1.8	0.80	1.44	0.887	0.81	1.46	0.840	0.770	1.39	0.817	0.78	1.40	0.807	0.78	1.40	0.803	0.77	1.38	0.821
1.6	0.84	1.34	0.837	0.85	1.36	0.782	0.820	1.31	0.782	0.82	1.31	0.762	0.82	1.31	0.755	0.79	1.26	0.750
1.4	0.89	1.24	0.772	0.89	1.24	0.730	0.860	1.20	0.734	0.86	1.20	0.717	0.86	1.20	0.723	0.83	1.16	0.723
1.2	0.92	1.10	0.707	0.91	1.09	0.672	0.890	1.07	0.690	0.88	1.06	0.669	0.88	1.06	0.665	0.86	1.03	0.653
1.0	0.94	0.94	0.644	0.93	0.93	0.610	0.920	0.92	0.629	0.92	0.92	0.627	0.92	0.92	0.620	0.89	0.89	0.623
0.8	0.95	0.76	0.562	0.95	0.76	0.547	0.940	0.75	0.548	0.94	0.75	0.549	0.93	0.74	0.560	0.93	0.74	0.563
0.6	0.96	0.58	0.464	0.96	0.58	0.470	0.960	0.58	0.480	0.955	0.57	0.477	0.95	0.57	0.475	0.95	0.57	0.483
0.4	—	—	—	—	—	—	—	—	—	0.97	0.39	0.377	0.97	0.39	0.375	0.97	0.39	0.423

and analogously for a solution of 0.04 M $CuSO_4$ + 0.19 M $Na_4P_2O_7$,

$$c_{Cu^{2+}} \cong 10^{-11.6}\ M;\quad c_{[Cu(P_2O_7)]^{2-}} \cong 10^{-6.8}\ M;$$
$$c_{[Cu(P_2O_7)_2]^{6-}} \cong 4 \cdot 10^{-3}\ M.$$

Thus discharge of the $[Cu(P_2O_7)_2]^{6-}$ ions is the most probable, their concentration in the solution being greater than that of all the other ions in the complex mixture. The fairly high stability of the complex $[Cu(P_2O_7)_2]^{6-}$ (the instability constant of the ion $[Cu(P_2O_7)_2]^{6-}$ $K_2 = 0.22 \times 10^{-10}$ and that of the ion $[Cu(P_2O_7)]^{2-}$ $K_1 = 0.56 \times 10^{-6}$) indicates the possibility of a slow discharge.

The equilibrium potentials of the copper electrode in the electrolytes studied lie between 0.105 and −0.002 V, and the surface of the copper electrode is charged negatively in all cases*, since the discharging complexes are negatively charged, so that the chemical polarisation must reach considerable values. Taking into account the presence of concentration and chemical polarisation and allowing for the Esin effect (the influence of the ligand concentration on the potential), the following relationship between the polarisation and the current density for electrodeposition would be expected:

$$\Delta\varphi = a + b\log\frac{i\left(1 + n\frac{c_Q}{c_a i_{lim}} i\right)^n}{1 - \frac{i}{i_{lim}}}, \qquad (1)$$

where a = const., $b = \frac{2.3RT}{z_c F\alpha}$, z_c is the charge on the copper ions, $0 \leqslant \alpha \leqslant 1$, n is the coordination number of the discharging complex, c_Q the concentration of the discharging complex (i.e. $Cu(P_2O_7)_2^{6-}$), c_a the concentration of ligand ions (i.e. $P_2O_7^{4-}$), and i_{lim} the limiting current density, determined graphically.

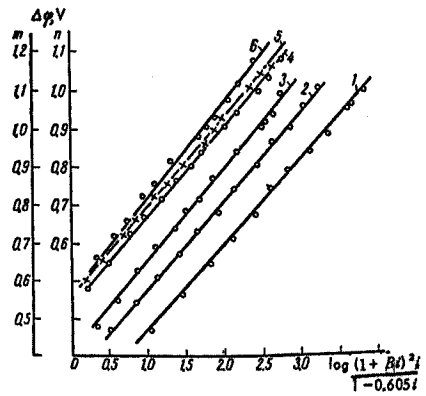

Fig. 1. Cathodic polarisation in copper pyrophosphate electrolytes: 1) c_a = 0.01 M; 2) c_a = 0.03 M; 3) c_a = 0.05 M; 4) c_a = 0.07 M; 5) c_a = 0.09 M; 6) c_a = 0.11 M.

For the discharge of $Cu(P_2O_7)_2^{6-}$ ions, Eqn. (1) takes the form

$$\Delta\varphi = a + b\log\frac{\left(1 + 1.21\frac{c_Q}{c_a} i\right)^2 i}{1 - 1.605\, i}$$

since i_{lim} = 1.65 mA/cm² for all the solutions studied, and n = 2. The factor 1.21 c_Q/c_a for solutions containing 0.09, 0.11, 0.13, 0.15, 0.17 and 0.19 M $Na_4P_2O_7$ is 4.72, 1.62, 0.98, 0.69, 0.54 and 0.44 respectively. Thus for the six electrolytes studied, the relationship between the polarisation and the current density is given by the equations**:

$$\Delta\varphi_1 = 0.240 + 0.230\log\frac{(1 + 4.72\, i)^2}{1 - 0.605\, i}\, i; \qquad (2)$$

* According to our measurements the potential of zero charge on copper in a pyrophosphate solution φ_N = 0.15 V.

** It should be noted that our earlier data [2] may be in error because of the presence of chloride ion in the electrolyte [4].

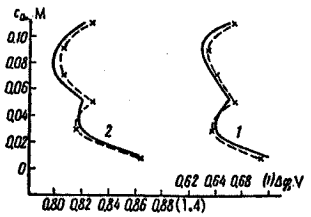

Fig. 2. Cathodic polarisation as a function of free pyrophosphate concentration. Solid lines are calculated from Eqns. (2)–(7); dotted lines are experimental data: 1) 1 mA; 2) 1.4 mA.

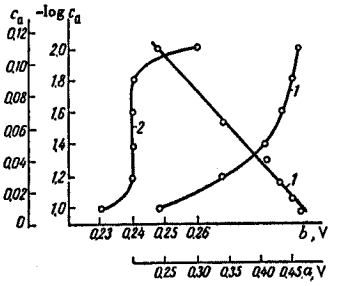

Fig. 3. The coefficients a (1) and b (2) as functions of free pyrophosphate concentration.

$$\Delta\varphi_2 = 0.340 + 0.24 \log \frac{(1 + 1.62\,i)^2}{1 - 0.605\,i}\, i; \quad (3)$$

$$\Delta\varphi_3 = 0.410 + 0.24 \log \frac{(1 + 0.97\,i)^2}{1 - 0.605\,i}\, i; \quad (4)$$

$$\Delta\varphi_4 = 0.430 + 0.240 \log \frac{(1 + 0.69\,i)^2}{1 - 0.605\,i}\, i; \quad (5)$$

$$\Delta\varphi_5 = 0.450 + 0.240 \log \frac{(1 + 0.54\,i)^2}{1 - 0.605\,i}\, i; \quad (6)$$

$$\Delta\varphi_6 = 0.460 + 0.26 \log \frac{(1 + 0.44\,i)^2}{1 - 0.605\,i}\, i. \quad (7)$$

The values of the constants a and b were found by the method of least squares, the value of the cathodic polarisation being taken as the most accurate variable, in accordance with the above.

Comparison of the experimental points with the theoretical curves (Fig. 1) shows that the latter describe quite accurately the dependence of the polarisation on the current density and on the concentration of free pyrophosphate (Fig. 2). The dependence of the cathodic polarisation on the concentration of $P_2O_7^{4-}$ at constant current density (Fig. 3) is fairly complex. This explains the contradictory results obtained by different investigators, who state on the one hand that the polarisation increases with increase of the $P_2O_7^{4-}$ concentration, and on the other that it decreases. From Fig. 3 it is clear that either effect may be observed.

We have earlier[2] ascribed the decrease in the polarisation with increase of the pyrophosphate concentration to a change in the constant a, but Fig. 3 shows that this assumption is unfounded. In fact this decrease appears as the result of the Esin effect [the coefficient $b = 2c_Q/c_a i_{lim}$ in Eqn. (1)] and of the dependence of the coefficient b in Eqn. (1) on the concentration. The graph also shows that in agreement with theory a is directly proportional to $\log c_a$. However, contrary to expectations, a increases rather than decreases with increase of $\log c_a$ and, moreover, the slope of the straight line (0.22) is considerably higher than the theoretical. This circumstance can only be due to the dependence of the ψ_1-potential on c_a. Thus Eqns. (2)–(7) may be replaced by

$$\Delta\varphi = 0.68 + 0.22 \log c_a + b \log \frac{(1 + Bi)^2}{1 - 0.605\,i}\, i, \quad (8)$$

where for c_a = 0.01, 0.03, 0.05, 0.07, 0.09, and 0.11 we have respectively B = 4.72, 1.62, 0.97, 0.69, 0.54 and 0.44; and b = 0.23, 0.24, 0.24, 0.24, 0.24, and 0.26.

The value of b is only slightly dependent on the concentration of free pyrophosphate. The experimental data show that b is independent of c_a in the range 0.03–0.09 M. Since

$$b = \frac{RT}{\alpha z_c F} = \frac{0.03}{\alpha},$$

the corresponding values for the coefficient α are

$$\alpha_1 = 0.130,\ \alpha_2 = \alpha_3 = \alpha_4 = \alpha_5 = 0.125,$$
$$\alpha_6 = 0.111.$$

These values are close to those which we obtained for concentrated pyrophosphate electrolytes[4] ($\alpha \cong 0.1$). An increase in the value of α at high concentrations of free pyrophosphate can scarcely be due to experimental errors, and is probably connected with a change in the distance between the metal surface and the minimum of the potential curve of the discharging ion in the complex. In general low values of α are typical of pyrophosphate electrolytes, and may be caused by the existence of a specific adsorption layer[4].

Copper Oxalate Electrolyte

We have studied the electrodeposition of copper from oxalate electrolytes at 25° in solutions of 0.01 M $CuSO_4$ + + 0.04 or 0.05 M $Na_2C_2O_4$. The results were almost identical with those found before[2], but the earlier interpretation was vitiated by neglect of the Esin effect. The limiting current density was 0.77 mA/cm² for both solutions. The

TABLE 2.

φ_{eq}, V	$\log a_{Cu}$	Γ	$\log\gamma_{ox}$	x_1	x_2	c_{ox}	c_1	c_2
0.132	−7.11	0.07	−0.39	0.126	15.85	0.0214	0.0037	0.0063
0.123	−7.42	0.09	−0.43	0.056	7.08	0.0338	0.0019	0.0081

TABLE 3. Cathodic polarisation in the deposition of copper from oxalate solutions.

i, mA/cm²	$c_{Na_2C_2O_4}$ = 0.04M; φ_1 = 0.132V			$c_{Na_2C_2O_4}$ = 0.05M; φ_2 = 0.123V		
	$\Delta\varphi$	$\log R(i)$	$\log Q(i)$	$\Delta\varphi$	$\log R(i)$	$\log Q(i)$
0.27	0.126	−0.223	−0.333	0.104	−0.257	−0.365
0.36	0.140	0.038	−0.105	0.116	−0.007	−0.147
0.45	0.155	0.285	0.112	0.127	0.232	0.061
0.54	0.167	0.550	0.348	0.139	0.485	0.288
0.64	0.188	0.919	0.687	0.153	0.850	0.617
0.73	0.221	1.532	1.275	0.178	1.457	1.197

current yield at current densities below the limiting value was almost 100%.

To obtain the equation for the cathodic polarisation, the ionic composition of the solutions must first be determined. The oxalic-acid anion is apparently able to form complexes with Cu^{2+}. The second instability constant of the complex has been determined by many workers and can be taken to be $K_2 = 1.2 \times 10^{-9}$.[2] The instability constant of the compound CuC_2O_4 may be evaluated as follows.

The stability of complex compounds is mainly determined by the charge, radius and electronic structure of the component ions. From this point of view, the stability of the complexes of Cu^{2+} with $C_2O_4^{2-}$ must be intermediate between the stabilities of the oxalate complexes of nickel and zinc.

The successive instability constants are connected by a definite relationship, which is expressed either by the Babko equation[5],

$$\log K_2 = \alpha \log K_1,$$

or by the van Panthaleon van Eck equation[6],

$$\log K_2 = \beta + \log K_1.$$

For the oxalate complexes of nickel, $\log K_2 = -6.5$ and $\log K_1 = -5.3$; consequently $\alpha_{Ni} = 1.23$ and $\beta_{Ni} = -1.20$.

For the oxalate complexes of zinc, $\log K_2 = -7.4$ and $\log K_1 = -4.9$; consequently $\alpha_{Zn} = 1.51$ and $\beta_{Zn} = -2.50$.[8]

Assuming that

$$\alpha_{Cu} \cong \frac{\alpha_{Ni} + \alpha_{Zn}}{2}; \quad \beta_{Cu} \cong \frac{\beta_{Ni} + \beta_{Zn}}{2},$$

we obtain $\alpha = 1.37$ and $\beta = -1.85$. Calculating the instability constant then gives $\log K_1 = -6.30$ from Babko's equation, and $\log K_1 = -6.85$ from van Panthaleon van Eck's equation; the average $\log K_1 = -6.6$*.

Using the equations

$$\log c_1 = \log a_{Cu} + \log c_{ox} + \log \gamma_{ox} - \log K_1 = \log x_1 + \log c_{ox};$$
$$\log c_2 = \log a_{Cu} + 2\log c_{ox} + \log \gamma_{ox} - \log K_2 = \log x_2 + 2\log c_{ox};$$
$$c_1 + c_2 = 0.01,$$

and calculating the activity coefficients from the approximate Davies equation[8]

$$\log \gamma = -0.5 z^2 \left(\frac{\sqrt{\Gamma}}{1 + \sqrt{\Gamma}} - 0.20 \Gamma \right)$$

where Γ is the ionic strength of the solution, we can find the concentrations of $C_2O_4^{2-}$, CuC_2O_4, and $[Cu(C_2O_4)_2]^{2-}$ in the electrolytes (Table 2).

The term determining the magnitude of the Esin effect, assuming discharge of CuC_2O_4, is $\log(1 + 0.433i)$ and $\log(1 + 0.136i)$, and for discharge of $[Cu(C_2O_4)_2]^{2-}$ it is $\log(1 + 0.742i)^2$ and $\log(1 + 0.567i)^2$.

The results of the measurements and calculations are given in Table 3. The experimental points fit with the equations satisfactorily:

for the first solution

$$\log(1 + 0.433\,i) \text{ and } \log(1 + 0.136\,i),$$

or

$$\log(1 + 0.742\,i)^2 \text{ and } \log(1 + 0.567\,i)^2;$$

for the second solution

$$\Delta\varphi_1 = 0.138 + 0.054 \log R(i)$$

$$\Delta\varphi_1 = 0.146 + 0.060 \log Q(i),$$

or

$$\Delta\varphi_2 = 0.116 + 0.043 \log R(i)$$

$$\Delta\varphi_2 = 0.122 + 0.049 \log Q(i),$$

where

$$\log R(i) = \log \frac{(1 + 0.742\,i)^2\, i}{1 - 1.30\,i}; \quad \log \frac{(1 + 0.567\,i)^2\, i}{1 - 1.30\,i};$$

$$\log Q(i) = \log \frac{(1 + 0.433\,i)\, i}{1 - 1.30\,i}; \quad \log \frac{(1 + 0.136\,i)\, i}{1 - 1.30\,i}.$$

According to Gauss's criterion, the best approximation is given by the equation for which the sum of the squares of the deviations in the values of φ is a minimum, i.e. $\Omega = \Sigma\delta\varphi^2 = \min$.

This condition is best satisfied when experimental data described by the equations based on the discharge of $[Cu(C_2O_4)_2]^{2-}$ anions are used*. However, the fact that the limiting current density is independent of the composition of the solution and of the concentration of the $[Cu(C_2O_4)_2]^{2-}$ ions is obscure. It may be due to the great increase in the excess of $C_2O_4^{2-}$ ions in the layer next to the cathode during steady-state electrolysis, so that the concentration of CuC_2O_4 is much lower here than in the bulk.

For the oxalate solutions, an increase in the ligand-ion concentration causes a decrease in the constant a from 0.136 to 0.116 V and an increase in the slow-discharge constant α, which is 0.56 for the first solution and 0.70 for the second.

SUMMARY

1. The cathodic polarisation in a series of copper pyrophosphate electrolytes has been studied. The polarisation is determined by concentration polarisation, by the Esin effect, and by the slow discharge. The slow-discharge constant for these solutions has very low values and depends on the composition of the solution. Discharge of $[Cu(P_2O_7)_2]^{6-}$ ions is the most probable.

2. The cathodic polarisation in a series of copper oxalate electrolytes has also been studied. Discharge of $[Cu(C_2O_4)_2]^{2-}$ ions is the most probable, and the slow-discharge constant depends on the composition of the solution, increasing with increase of the oxalate concentration.

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* These results seem to be inconsistent (Ed. of Translation).

* If the Esin effect is ignored, as was done earlier [2], Gauss's criterion is of the order $(40\text{-}50) \times 10^{-3}$, i.e. it is 10-15 times greater than for Eqn. (1).

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SUBSTITUTION OF HYDROGEN ATOMS IN THE BENZENE RING BY ALKYL GROUPS. VII. THE RATIO BETWEEN THE VELOCITY CONSTANTS FOR THE FORMATION OF ISOPROPYLBENZENES AND EQUATIONS FOR THE COMPOSITION OF THE PRODUCTS OF THE ALKYLATION OF BENZENE WITH PROPYLENE IN THE PRESENCE OF ALUMINIUM CHLORIDE

V. G. Plyusnin, E. P. Babin, M. I. Nasakina, and N. M. Rodigin

It has been shown[1-3] that when benzene is alkylated with propylene in the presence of 96–98% hydrogen fluoride, a series of reactions takes place, with the formation of mono-, di-, tri-, and tetraisopropylbenzenes, in which the ratios between the velocity constants for the formation of the successive alkylbenzenes $k_1 : k_2 : k_3 : k_4 = 1 : 0.8 : 0.32 : 0.16$.

When aluminium chloride is used as catalyst, the successive reactions also occur[4,5]; we thought it of interest to determine the ratio between the successive velocity constants for the formation of the alkylbenzenes in the propylation of benzene with aluminium chloride, using the appropriate kinetic equations[1,6].

To study the kinetics of the reaction in the presence of aluminium chloride, benzene was exhaustively alkylated with propylene at 60°. All experiments were carried out with dry chemically pure benzene (d_4^{20} 0.8788, n_D^{20} 1.5017) and 96–98% propylene obtained by the dehydration of isopropyl alcohol over alumina.

EXPERIMENTAL

Benzene was alkylated in a three-necked flask fitted with a condenser, a stirrer, and a gas bubbler for the passage of propylene.

The propylene was passed from a gasometer through a drying train at constant velocity, such that the gas was almost completely absorbed in the system; this was usually 300–330 litres per hour per kg of benzene. The stainless steel spiral stirrer was rotated at 2000–2500 r.p.m. The reaction temperature was maintained at 60° ± 0.2° in a water thermostat. 300 g of benzene and 38.4 g of catalyst (0.03 mole per mole benzene) were used in all the experiments.

The products, including those separated from the catalyst layer after washing and drying, were distilled with a column of 30 theoretical plates, which was sufficient to achieve a clear separation between benzene and the alkylbenzenes because of the fairly large difference in their boiling points. The intermediate fractions, which did not amount to more than 1–1.5% of the alkylbenzenes, were divided equally between the neighbouring alkylbenzenes.

TABLE 1. Alkylation of benzene with propylene at 60°.

n	p_0	p_1	p_2	p_3	p_4	y
0.208	71.9	20.4	—	—	—	10.11
0.390	48.9	37.6	—	—	—	17.36
0.493	45.6	37.1	5.2	—	—	20.98
0.589	38.9	43.6	—	—	—	24.08
0.660	32.5	47.2	8.8	—	—	26.22
0.756	29.6	47.9	13.3	—	—	28.93
0.832	22.6	52.1	14.8	—	—	30.94
0.891	23.3	49.2	15.0	—	—	32.42
1.000	19.0	47.2	25.0	2.1	—	35.00
1.178	12.7	44.3	30.8	—	—	38.81
1.268	9.6	38.1	37.5	—	—	40.57
1.405	8.8	33.7	41.2	—	—	43.07
1.492	5.6	31.8	45.0	13.5	—	44.55
1.820	2.8	21.6	49.2	—	—	49.49
1.838	2.5	18.5	51.2	13.0	—	—
2.007	1.8	13.1	50.4	18.1	—	51.94
2.118	1.3	10.8	50.0	27.0	—	53.28
2.473	0.7	3.3	41.6	40.4	9.2	57.11
2.572	0.5	2.2	31.7	54.5	—	58.07
2.722	0.6	0.8	24.4	62.4	—	59.44
2.929	0.3	0.1	8.2	78.6	—	61.19
3.047	0.6	—	4.5	82.8	10.5	62.13
3.091	2.3	0.2	0.6	87.8	5.4	62.47
3.247	0.5	0.5	0.9	74.1	20.1	63.62
3.308	0.6	—	1.3	79.4	15.8	64.04
3.438	1.2	—	1.0	57.2	36.5	64.93

Table 1 gives the weight composition of the alkylation products with various molar ratios n of propylene to benzene; p_0 is the benzene content of the product in wt.%, p_1, p_2, p_3, and p_4 are the contents of mono-, di-, tri-, and tetraisopropylbenzenes in the product in wt.%, and y is the calculated amount of propylene used in the formation of the alkylbenzenes, based on the percentage composition of the catalysate.

DISCUSSION

The olefin balance[2] obtained from the molar ratio n and the distillation products shows that the quantity of polymeric products Δy in the system is very small, and has practically no effect on the experimental molar ratios n; hence the data of Table 1 were used directly to determine the ratio between the velocity constants of the successive reactions.

By a suitable choice of constants a_i[1,6], it was found that the closest fit between the experimental and the calculated data is obtained with the ratios $k_1 : k_2 : k_3 : k_4 = 1 : 0.58 : 0.24 : 0.015$ and that the equations for the composition have the form (with $k_1 = k$)

$$c_0 = 100\, e^{-kt},$$
$$c_1 = 100\,(2.381\, e^{-0.58kt} - 2.381\, e^{-kt}),$$
$$c_2 = 100\,(2.245\, e^{-0.24kt} - 4.062\, e^{-0.58kt} + 1.871\, e^{-kt}),$$
$$c_3 = 100\,(1.112\, e^{-0.015kt} - 2.354\, e^{-0.24kt} + 1.725\, e^{-0.58kt} - 0.443\, e^{-kt}),$$
$$c_4 = 100\,(1 - 1.112\, e^{-0.015kt} + 0.152\, e^{-0.24kt} - 0.024\, e^{-0.58kt} + 0.047\, e^{-kt}),$$
$$\sum_{c_0}^{c_4} c_i = 100. \qquad (1)$$

Since $n = (1c_1 + 2c_2 + 3c_3 + 4c_4)/100$, substituting the values of c_i from Eqn. (1), we obtain n as a function of kt (Table 2):

$$n = 4 + 0.220\, e^{-kt} - 0.744\, e^{-0.58kt} - 2.084\, e^{-0.24kt} - 1.112\, e^{-kt}. \qquad (2)$$