

nitro-1,3,4-trihydroxy benzene pyrocatechol cannot be used for nitration because of its facile oxidation. Resorcinol too was a poor choice for nitration experiment because in resorcinol, it is the β -position that is more reactive towards substitutions rather than the γ -position. Good yields of γ -substituted resorcinol derivatives are difficult to realise. Resacetophenone also leads to electrophilic substitutions in position 5 by most of the conventional reagents. In our experiments towards biomimetic hydroxylations, we have achieved the synthesis of 2,4-dihydroxy-3-nitro-acetophenone in good yield by the reaction of cerium (IV) ammonium nitrate, a well documented reagent for oxidations^{6,7} and oxidative acetoxylation^{8,9}. 2,4-dihydroxy-3-nitroacetophenone can then be conveniently oxidised by Baeyer Villiger reactions to yield 2-nitro-1,3,4-trihydroxy benzene, a model for tetrahydroxy benzenes.

This communication is the first one pot facile synthesis of 2,4-dihydroxy-3-nitroacetophenone in good yields. Further work on the mechanism and applications of the reagent for oxidation in hydrophobic and hydrophilic phases is in progress.

Resacetophenone (2 g) in acetic acid (5 ml) was added to a solution of cerium (IV) ammonium nitrate in acetic acid (5 g, 30 ml) and the reaction mixture heated in water bath (50–60°, 5 min). The progress of the reaction was followed by TLC; on its completion (20 min) the reaction mixture was poured on to crushed ice (50 g) and extracted with benzene, the organic layer on concentration left a solid which was column chromatographed (silica-gel) using petroleum ether and benzene for elution. A shining yellow compound A was obtained from the petroleum ether-benzene (95:5) eluate which melted at 90–91° C, gave positive Lassaigne's test for nitrogen and positive ferric reaction for phenols. It showed strong absorptions at 3200 cm^{-1} (-OH group) and 1520, 1320 cm^{-1} (nitro group) in its IR spectrum and a two proton singlet at δ 12.4 attributable to two phenolic protons; a two proton multiplet at δ 8.0 assignable to aromatic protons and a singlet at δ 2.6 integrating for 3 protons (COCH_3) in its PMR spectrum. The identity of compound A was established as 2,4-dihydroxy-3-nitro-acetophenone by comparison with its literature data (lit m.p. 93° C). Compound A on treatment with $\text{H}_2\text{O}_2/\text{OH}^-$ gave 2-nitro-1,3,4-trihydroxy benzene (m.p., m.m.p., Co-IR and Co-TLC) with authentic sample in 20% yield.

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KINETICS OF AQUATION OF BROMOPENTA-AMMINECOBALT (III) PERCHLORATE IN DICARBOXYLATE SOLUTIONS CONTAINING 10% ETHANOL AT 40° C.

M. F. AMIRA*, F. M. ABDEL-HALIM, N. H. ISMAIL AND M. M. ELSEMONGY†
Chemistry Department, Faculty of Science, Alexandria University, Egypt.

*Present address: Chemistry Department, Faculty of Science, Sana'a University, Yemen Arab Republic.

† Chemistry Department, Faculty of Science, Mansoura University, Egypt.

RECENTLY Amira, *et al*¹ surveyed studies on the rate of aquations of chloro- and bromo-penta-amminecobalt (III) and of penta-amminechromium (III) in aqueous and also in the presence of 10% ethanolic solutions of sulphate and dicarboxylates. They found an exception in the empirical correlation between $k(\text{ion-pair})/k(\text{ion})$ (k_{ip}/k_i) ratio and the dissociation constants (K) for the dicarboxylate series in the case of aquation of bromopenta-amminecobalt (III) ion in 10% ethanolic dicarboxylate solutions. This was attributed to the consequence of using a mixed solvent.

In our present investigation, a comprehensive study was undertaken on the kinetics of aquation of bromopenta-amminecobalt (III) perchlorate in 10% ethanolic dicarboxylate solutions to solve the above exception.

Bromopenta-amminecobalt (III) bromide was prepared² and converted to perchlorate from warm acid-

TABLE 1

Values of rate coefficients of aquation of bromopenta-amminecobalt (III) ion in different dicarboxylate media containing 10% ethanol at 40° C.

$$(10^3 k_1 = 1.88 \pm 0.10 \text{ min}^{-1})$$

Buffer (10 ³ K)*	10 ³ C ₁	10 ³ C	_B 10 ³ C	10 ⁴ CpL	10 ³ k _{obs} (min ⁻¹)	10 ³ k _{ip} (min ⁻¹)	k _{ip} k ₁
Malonate (3.5)	7.3	12.1	3.06	8.9	2.90 ± 0.15	5.39	2.32
	10.9	18.2	2.80	10.0	2.98 ± 0.17	4.97	
	14.5	24.2	3.08	12.1	2.78 ± 0.08	4.17	
	16.3	27.3	3.03	12.4	2.60 ± 0.10	3.64	
	21.8	36.3	2.81	12.6	2.66 ± 0.13	3.62	
Succinate (6.3)	14.5	24.2	2.84	7.9	2.88 ± 0.07	5.46	2.58
	16.3	27.3	3.27	9.4	2.62 ± 0.06	4.45	
	21.8	36.3	3.98	9.6	2.77 ± 0.07	4.65	
	26.0	45.0	3.04	10.7	2.93 ± 0.10	4.86	
Tartrate (4.0)	21.8	36.3	2.93	8.1	3.08 ± 0.10	6.21	3.11
	24.5	40.0	3.14	8.8	2.92 ± 0.04	5.59	
	26.0	45.0	3.02	9.2	2.87 ± 0.15	5.12	
	40.0	50.0	2.95	6.9	2.87 ± 0.08	6.12	
	48.0	60.0	2.99	7.4	2.76 ± 0.15	5.43	
	50.5	55.0	2.86	7.0	2.93 ± 0.05	6.15	
Maleate (1.50)	7.3	12.1	2.70	11.8	3.53 ± 0.05	5.66	3.17
	10.9	18.2	2.87	14.7	4.24 ± 0.14	6.47	
	14.5	24.3	2.87	15.6	4.00 ± 0.04	5.66	
	21.8	36.3	2.32	14.4	4.10 ± 0.45	5.46	
	24.5	40.0	2.93	18.1	4.75 ± 0.15	6.53	
Phthalate** (1.10)	22.0	18.2	2.99	19.4	5.32 ± 0.16	7.02	3.82
	29.1	24.2	2.83	20.2	6.02 ± 0.16	7.69	
	32.7	27.1	3.10	22.8	5.28 ± 0.08	6.51	
	43.6	36.3	2.93	22.4	6.32 ± 0.16	7.69	
	80.0	50.0	2.88	23.9	6.10 ± 0.28	6.97	

* Values of K were taken from reference (1)

** C₁ = Pot. hydrogen phthalate.

fied solution of concentrated LiClO₄ by cooling in ice. The product was washed until free from acid using alcohol and ether and then dried over silica gel [Anal. Calcd. for perchlorate, is 47.07%; Found, 46.86%]. AnalaR grade chemicals were used for making stock solutions of the ion-pairing ligands.

The rate of reaction was followed potentiometrically, using timed samples cooled by ice-water³.

The catalytic effect of dicarboxylate ligands on the rate of aquation of bromopenta-amminecobalt (III) perchlorate was studied with five different dicarboxy-

late ligands namely, succinate tartrate, malonate, maleate and phthalate. For each ligand four or more kinetic runs were performed in which the buffer composition was varied over a wide range. The observed first order rate constants, k_{obs}, were calculated from the potentiometric titration readings by linear least from the mean square analysis of ln V_∞ - (V_∞ - V_t), t data (V_t = titration at time t and V_∞ = infinity titration). Values of k_{obs} for different dicarboxylate ligands are given in the table. As in previous cases^{4,5}, the data were analysed using the Wyatt-Davies treatment in the form

$$k_{\text{obs.}} C = k_1 (C - [\text{CpL}]) + k_{\text{ip}} [\text{CpL}] \quad (1)$$

where C the stoichiometric concentration of the complex salt and $[\text{CpL}]$ represents the ion-pair concentration; k_{ip} and k_1 are ion-pair and the uncatalysed rate constants respectively.

The values of $[\text{CpL}]$ were calculated from (2). The method of calculation has been described previously⁵.

$$[\text{CpL}]^2 - [(C + C_A - [\text{HL}] - [\text{H}_2\text{L}]) + K/f_2] [\text{CpL}] + \alpha C_A - [\text{HL}] - [\text{H}_2\text{L}] = 0 \quad (2)$$

C_A and C_B and the stoichiometric concentrations of the dicarboxylic acid and sodium hydroxide respectively while f_1 and f_2 are the activity coefficients of uni- and divalent ions. k_{ip} were calculated using (1).

The kinetic data for different experimental conditions, beside the mean values of k_{ip}/k_1 are shown in the table given, while figure 1 shows the plot of k_{ip}/k_1 against K for five different dicarboxylates (solid circles) which seems now to be mixed with the other

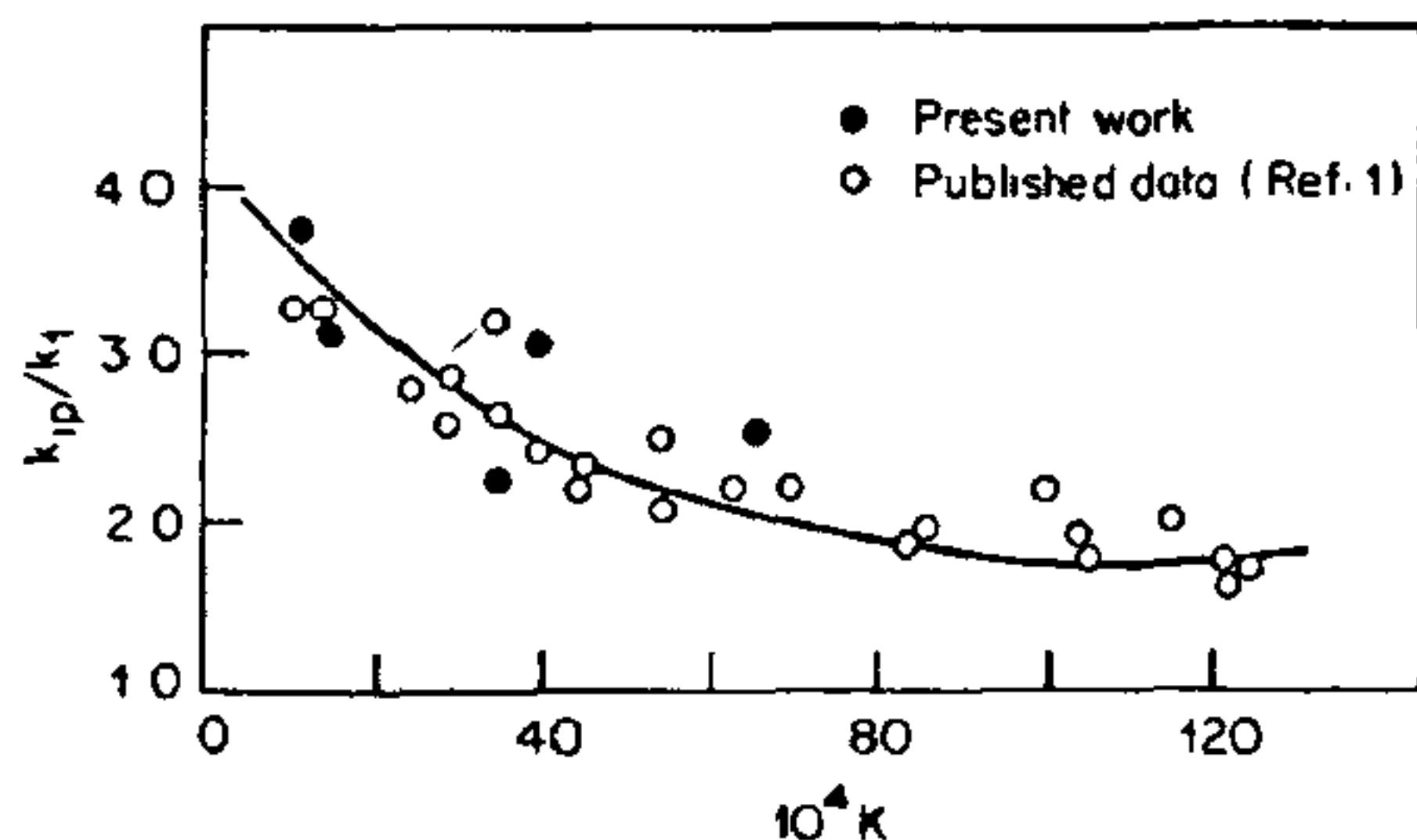


Figure 1. Plot of k_{ip}/k_1 ratios against K values.

published data¹ (open circles) and this conclusion solves the problem created before¹ as a result of the higher scattered values of k_{ip}/k_1 in the empirical correlation with K . Due to the new finding, a smooth curve could now connect the different points in figure 1 for different complexes in different dicarboxylate media.

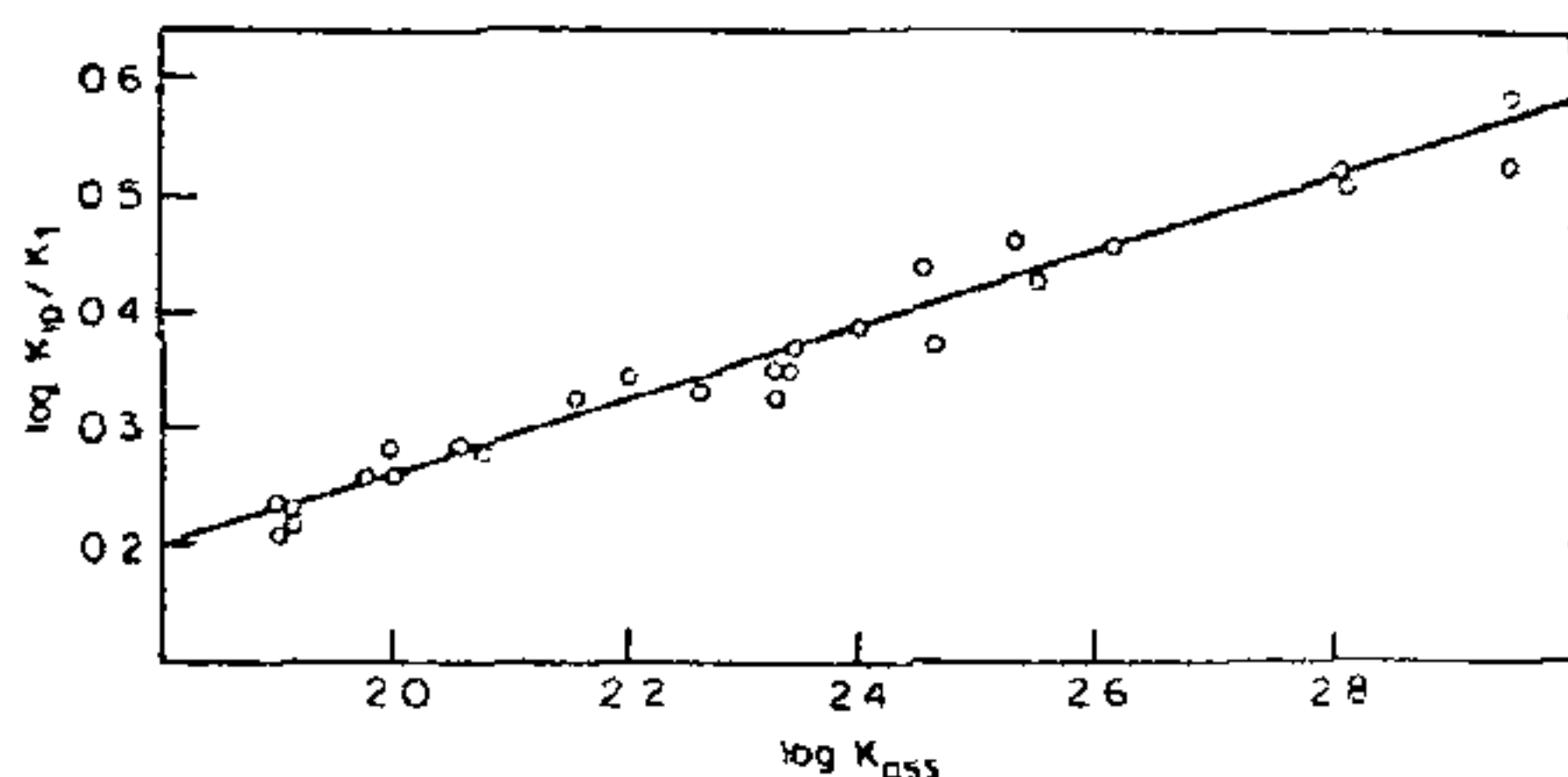


Figure 2. Dilogarithmic plot of k_{ip}/k_1 and K_{ass} for different dicarboxylate media.

A new empirical correlation between k_{ip} , k_1 and K_{ass} has been tested by analysing the data in figure 1, where the dilogarithmic plot of k_{ip}/k_1 and K_{ass} gives a straight line as shown in figure 2; the correlation coefficient being 0.981. This new correlation which fits for most of the data in figure 1, can be represented as,

$$k_{\text{ip}} = 0.502 k_1 K_{\text{ass}}^{0.28}$$

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SIGNIFICANCE OF ALBITE RIMS AROUND FELSPARS IN THE MIGMATITES OF SARAHAN BUSHAIR AREA, HIMACHAL PRADESH, INDIA.

K. P. SINGH

Centre of Advanced Study in Geology, Punjab University, Chandigarh 160 014, India.

RIMS of albite ($\text{An}_4\text{-An}_9$) have been observed around oligoclase and the potash feldspars in the migmatites around Sarahan Bushair ($31^\circ 30' 27''$: $77^\circ 47' 58''$) in Himachal Pradesh. The migmatites belong to Jutogh Formation and have been classified into foliated-, augen-, biotite gneiss and leucocratic muscovite gneiss¹. Petrographic features like sericitization, decalcification, antiperthitic, perthitic, albite rims around plagioclase and potash feldspars and myrmekitic intergrowths, etc have been observed. The migmatites were formed by metasomatic migmatization of metapelitic, metasemipelitic and metapsammitic country rocks¹.

Megascopically, the albite rims are not clearly visible. In thin sections, these are commonly seen in augen migmatites and biotite gneisses, encircling the plagioclase feldspar ($\text{An}_{18}\text{-An}_{27}$) (figure 1) and K-feldspar and measuring in thickness from 0.07–0.16