136. *Equilibrium Constants in Terms of Activities (Cryoscopic). Part VI. Pyridine* p-*Chlorophenoxide in Benzene and in* p-*Dichlorobenzene.*

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THE freezing point–composition diagram for the system pyridine–*p*-chlorophenol exhibits a very sharp maximum at the point corresponding to the compound pyridine *p*-chlorophenoxide, which shows pronounced super-cooling (J., 1936, 789). These facts suggest that the compound has marked stability, and therefore the equilibrium constants of its dissociation in benzene and in *p*-dichlorobenzene have been determined by the methods already described (J., 1936, 1303, and earlier references). The exceptionally small heat of formation of the compound is discussed.

Purification of materials and the experimental cryoscopic method were as before (*loc. cit.*). The table and the figure give the results of the present work.

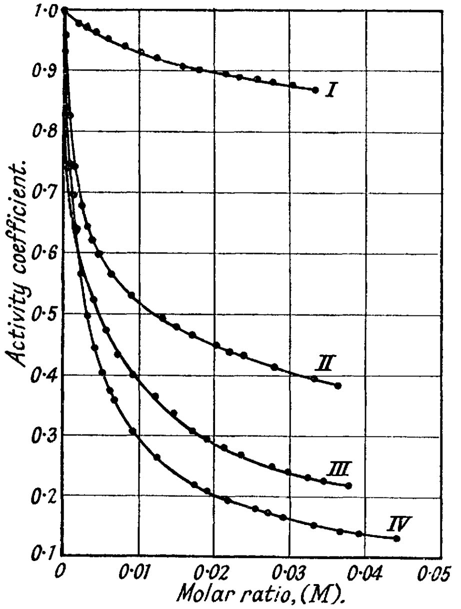
Heat of Formation.—The average values of K_a (table) have been applied in the isochore (cf. Part II, J., 1933, 1431), whence the heat of formation of pyridine *p*-chlorophenoxide has been found to be $Q = -480$ cals., the compound being formed exothermally.

Equilibrium constants and activity coefficients for benzene and p-*dichlorobenzene solutions of pyridine* p-*chlorophenoxide at molar ratio* = M.

(γ_A, γ_B, γ_{AB} = activity coefficient of pyridine, *p*-chlorophenol, and undissociated pyridine *p*-chlorophenoxide, respectively.)

$10^3 \times M$.	ΔT.	K_a.	γ.	γ_A.	γ_B.	γ_{AB}.	$10^3 \times M$.	ΔT.	K_a.	γ.	γ_A.	γ_B.	γ_{AB}.
(a) *Benzene solutions.*													
0·510	0·061°	443·8	0·838	0·957	0·997	0·993	12·38	0·927°	444·1	0·262	0·852	0·973	0·528
0·960	0·109	446·0	0·747	0·939	0·994	0·984	17·43	1·241	444·9	0·219	0·839	0·967	0·494
1·364	0·149	442·1	0·691	0·925	0·992	0·950	19·05	1·341	446·0	0·208	0·836	0·966	0·475
1·701	0·179	444·0	0·640	0·922	0·991	0·945	21·76	1·500	443·5	0·194	0·831	0·963	0·465
2·301	0·225	444·0	0·565	0·912	0·990	0·837	25·22	1·701	442·2	0·179	0·827	0·961	0·448
3·218	0·296	441·0	0·493	0·906	0·986	0·735	27·14	1·812	443·2	0·172	0·824	0·960	0·438
4·114	0·362	442·5	0·441	0·902	0·984	0·689	29·08	1·919	442·8	0·165	0·819	0·958	0·433
5·103	0·440	442·7	0·400	0·883	0·982	0·644	33·79	2·173	444·0	0·151	0·815	0·956	0·413
6·131	0·514	443·6	0·372	0·880	0·980	0·623	36·55	2·323	443·6	0·144	0·812	0·955	0·403
6·676	0·549	446·4	0·355	0·878	0·979	0·607	39·06	2·454	444·3	0·138	0·810	0·954	0·392
9·092	0·711	444·4	0·305	0·862	0·977	0·565	41·98	2·607	446·4	0·133	0·806	0·952	0·389
(b) p-*Dichlorobenzene solutions.*													
1·484	0·121	393·2	0·708	1·004	1·000	0·990	21·80	1·311	394·3	0·275	1·057	0·972	0·910
2·874	0·217	394·1	0·614	1·014	0·996	0·985	24·28	1·443	394·2	0·262	1·060	0·971	0·906
4·352	0·304	392·1	0·514	1·028	0·992	0·980	28·13	1·646	396·9	0·246	1·064	0·968	0·897
6·061	0·417	393·4	0·465	1·034	0·991	0·973	30·20	1·752	395·4	0·225	1·068	0·966	0·893
7·877	0·524	396·0	0·425	1·040	0·986	0·965	32·89	1·893	392·1	0·223	1·070	0·964	0·887
9·749	0·639	392·3	0·391	1·044	0·985	0·953	35·10	2·003	394·2	0·220	1·071	0·962	0·882
12·52	0·800	394·1	0·356	1·048	0·982	0·941	38·11	2·151	394·1	0·211	1·074	0·958	0·877
15·20	0·951	394·0	0·330	1·053	0·978	0·930	42·33	2·362	392·7	0·195	1·076	0·954	0·869
17·73	1·092	394·0	0·300	1·056	0·976	0·923							

Average values of K_a: in benzene, 443·8; in *p*-dichlorobenzene, 394·0.



I and III, dichlorobenzene solutions.
II and IV, benzene solutions.
I and II, undissociated pyridine *p*-chlorophenoxide (γ_{AB}).
III and IV, pyridine and *p*-chlorophenol together in solution (γ).

DISCUSSION.

The present values of K_a are much larger than those previously reported (*loc. cit.*) for other amine–phenol compounds, particularly in *p*-dichlorobenzene solutions. This indication of considerable stability in pyridine *p*-chlorophenoxide might be expected from a consideration of the dipole moments of the components of the compound, *viz.*, pyridine, 2·2; *p*-chlorophenol, 2·3 (*Trans. Faraday Soc.*, 1934, **30**, Appendix), but, contrary to expectation, the heat of formation ($Q = -480$ cals.) is much less than any of those reported previously; compare especially pyridine *o*-chlorophenoxide, $Q = -6800$ cals. (Part II, J., 1933, 1431). The difference between these two heat values can scarcely be ascribed to some special property of *p*-chlorophenol, since the corresponding chlorophenoxides of *p*-toluidine have heats of formation which do not greatly differ (Part V, J., 1936, 1302). Marked differences in heats of formation of amine–phenol compounds do not seem to accord with the idea that a well-defined link, N$\rightharpoondown$H, is formed in all such compounds (cf. Part IV, J., 1934, 1292).

The properties of benzene and *p*-dichlorobenzene were discussed (Part II, *loc. cit.*), and it was considered that these two substances were solvents which provide similar thermodynamic environments. Hence specific solvent influences, as a cause of very small heat effects, are assumed to be of a very subsidiary nature. An examination of the data reported in earlier parts of the present series of papers reveals no evidence of such specific influences.

The relative lengths of the dipoles of component molecules in compounds may be expected to influence the type of combination and hence the heats of formation. Bernal (*Trans. Faraday Soc.*, 1934, **30**, 776), considering the association of alcohols, suggested that two types of complex may be formed, *viz.*, polar and non-polar. A similar difference may exist between pyridine *p*-chlorophenoxide and its *o*-chlorophenoxide, the former being a polar compound. The very different dipole lengths of *p*-chlorophenol and pyridine may account for the formation of such a polar compound, which, in turn, may account for the small heat of formation of pyridine *p*-chlorophenoxide now reported. Such explanation is speculative, and a precise interpretation of the results in this series of papers cannot be put forward at present.

SUMMARY.

The equilibrium constant, $K_a = a_{AB}/a_A a_B$, has been calculated for the dissociation of pyridine *p*-chlorophenoxide in benzene and in *p*-dichlorobenzene solutions. Average values of K_a have been found for the two mean temperatures, $T = 277{\cdot}0°$ and $T = 324{\cdot}3°$, and the van't Hoff isochore has been applied to calculate the heat of formation of pyridine *p*-chlorophenoxide. This heat of formation is quite small compared with those previously reported, and a possible explanation has been discussed.

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