279. *Equilibrium Constants in Terms of Activities (Cryoscopic). Part IV. The Dissociation of* p-*Toluidine* o-*Tolyloxide in Benzene and in* p-*Dichlorobenzene.*

By H. M. Glass and W. M. Madgin.

In earlier parts of this series (this vol., p. 261 and earlier references) it was found that pyridine and quinoline *o*-chlorophenoxides have the same heat of formation, and this was ascribed to the existence of a co-ordinate linkage between the nitrogen atom in the base and the hydrogen in *o*-chlorophenol. Without apparently altering the co-ordinate link, the effects of substitution may be studied by considering such a molecular compound as that of *p*-toluidine and *o*-cresol (Pushin and Sladovic, J., 1928, 2474), in which CH_3 is substituted for Cl, and the base is primary instead of tertiary.

MacLeod (*Trans. Faraday Soc.*, 1934, **30**, 482) has calculated heats of formation of several similar *o*-chlorophenoxides and finds widely varying values: also, the value for any one compound decreases considerably with rise of temperature. He considers the values for the highest temperatures to be the most reliable, and these approach most nearly to the values found by us.

The object of the present investigation was to determine whether compounds of these types all contain the same fundamental linkage.

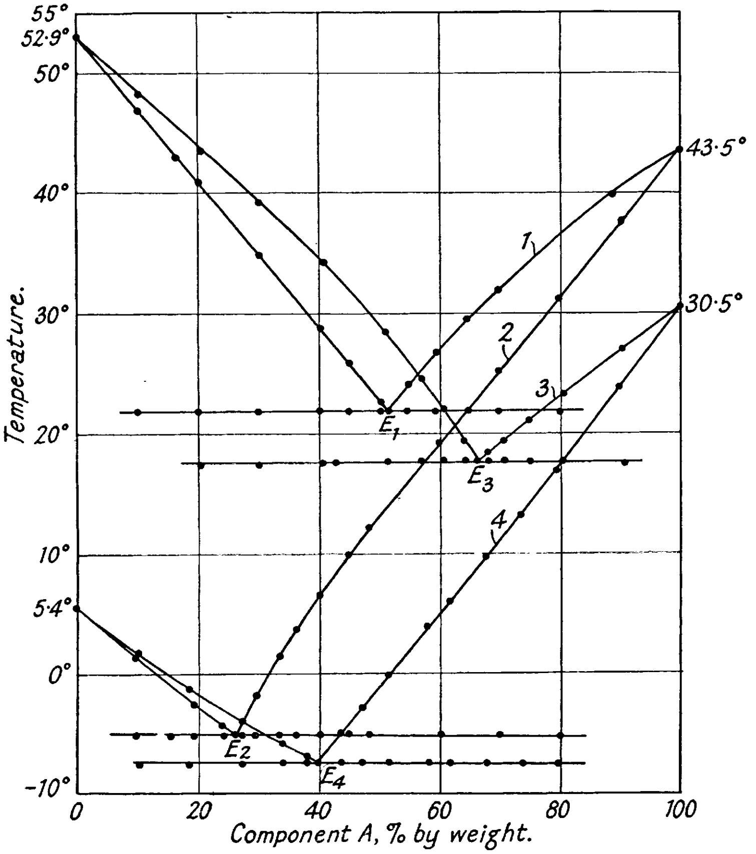
EXPERIMENTAL.

p-Toluidine was recrystallised twice from dry ligroin, dissolved in ether, and kept over potassium hydroxide for several days; after evaporation of the ether, the *p*-toluidine was distilled under reduced pressure; m. p. 43·5°. *o*-Cresol was purified as by Dawson and Mountford (J., **1918, 113,** 923); m. p. 30·5°. Other substances were as before (*loc. cit.*).

Binary Systems.—As before (*loc. cit.*), it was necessary that the solutes selected should form eutectic systems with both of the solvents. The four binary systems formed by the two solvents with *p*-toluidine and with *o*-cresol were therefore first investigated and found to be of the eutectic type (see Fig. 1). The methods of investigation were as previously described (this vol., p. 260) and, whenever possible, the melts were inoculated with the appropriate solid phase to prevent supercooling. It was possible to isolate solid phases from most melts (cf. Fig. 1), and the m. p.'s of these solids showed that they were practically pure components, thus confirming the eutectic type.

FIG. 1.

Freezing point–composition diagrams.



	1.	2.	3.	4.
A.	p-*Toluidine*	p-*Toluidine*	o-*Cresol*	o-*Cresol*
B.	p-*Dichlorobenzene.*	*Benzene.*	p-*Dichlorobenzene.*	*Benzene.*

E_1 51·5% A (21·9°); E_2 26% A (−5·1°); E_3 66·5% A (17·7°); E_4 39·5% A (−7·4°).

Activity Coefficients.—Tables I and II give the results of the present work, and the experimental cryoscopic method was as before (*loc. cit.*). Fig. 2 shows certain similarities to previous results (*loc. cit.*). For instance, in *p*-dichlorobenzene solutions, certain activity coefficients are greater than unity and, in both solvents, γ_{AB} values are markedly low. These apparent abnormalities are discussed below.

TABLE I.

Activity coefficients for p-*toluidine and* o-*cresol as solutes.*

(M = Molar ratio of solute; ΔT = depression of freezing point.)

p-Toluidine as solute.

Benzene solutions.						*p*-Dichlorobenzene solutions.					
10^3M.	ΔT.	γ_A.	10^3M.	ΔT.	γ_A.	10^3M.	ΔT.	γ_A.	10^3M.	ΔT.	γ_A.
0·657	0·043°	0·997	13·49	0·866°	0·963	1·253	0·061°	1·002	15·90	0·759°	0·983
1·547	0·101	0·994	14·37	0·921	0·961	1·745	0·085	1·003	17·38	0·826	0·977
1·776	0·116	0·994	14·89	0·954	0·960	2·505	0·122	1·004	18·94	0·897	0·972
3·254	0·212	0·990	16·91	1·081	0·956	3·182	0·155	1·005	20·19	0·953	0·968
4·611	0·300	0·987	19·80	1·262	0·950	4·189	0·204	1·006	22·08	1·037	0·961
5·610	0·364	0·983	22·92	1·456	0·944	5·524	0·269	1·007	24·39	1·139	0·952
6·953	0·450	0·978	26·13	1·656	0·940	7·215	0·351	1·006	27·20	1·264	0·944
7·949	0·514	0·976	29·75	1·879	0·934	8·589	0·417	1·003	30·97	1·430	0·933
9·236	0·596	0·973	31·94	2·014	0·931	10·69	0·517	0·999	34·47	1·584	0·924
10·66	0·687	0·970	37·27	2·339	0·923	12·52	0·603	0·994	39·08	1·784	0·912
12·24	0·787	0·966				14·28	0·685	0·990	45·36	2·056	0·898

o-Cresol as solute.

10^3M.	ΔT.	γ_B.	10^3M.	ΔT.	γ_B.	10^3M.	ΔT.	γ_B.	10^3M.	ΔT.	γ_B.
1·012	0·066°	0·992	16·66	1·031°	0·895	0·945	0·046°	1·002	17·44	0·823°	0·970
1·462	0·095	0·986	18·51	1·137	0·884	1·662	0·081	1·006	18·86	0·885	0·963
2·758	0·179	0·981	20·71	1·264	0·873	2·787	0·136	1·008	19·78	0·925	0·958
3·483	0·225	0·974	22·99	1·392	0·861	3·422	0·167	1·009	21·44	0·997	0·950
4·424	0·285	0·968	24·33	1·468	0·854	4·490	0·219	1·010	24·16	1·113	0·937
5·877	0·377	0·959	27·02	1·616	0·841	5·480	0·267	1·009	26·92	1·228	0·923
7·336	0·468	0·949	29·49	1·752	0·831	6·827	0·332	1·008	29·29	1·326	0·912
9·45	0·598	0·935	33·02	1·942	0·815	8·330	0·404	1·006	31·34	1·411	0·903
10·28	0·649	0·931	36·18	2·110	0·802	10·01	0·483	1·000	35·44	1·581	0·887
11·79	0·740	0·921	41·05	2·364	0·783	11·54	0·555	0·995	39·20	1·735	0·874
13·56	0·846	0·911				13·73	0·656	0·987	43·12	1·896	0·862
						16·15	0·766	0·977			

TABLE II.

Equilibrium constants and activity coefficients for benzene and p-*dichlorobenzene solutions of* p-*toluidine* o-*tolyloxide at molar ratio* = M.

(γ_A, γ_B, and γ_{AB} = activity coefficients of *p*-toluidine, *o*-cresol, and undissociated complex respectively.)

Benzene solutions.

10^3M.	ΔT.	K_a.	γ.	γ_A.	γ_B.	γ_{AB}.	10^3M.	ΔT.	K_a.	γ.	γ_A.	γ_B.	γ_{AB}.
0·323	0·042°	—	0·987	—	—	—	9·257	1·065°	31·06	0·773	0·978	0·949	0·867
0·807	0·104	—	0·968	—	—	—	10·10	1·148	31·41	0·757	0·977	0·945	0·853
1·248	0·160	31·26	0·958	0·996	0·992	0·993	11·63	1·298	31·54	0·731	0·974	0·939	0·831
1·514	0·193	32·19	0·949	0·995	0·990	0·992	13·21	1·447	31·34	0·706	0·972	0·934	0·797
2·023	0·256	32·44	0·933	0·994	0·986	0·988	14·85	1·598	31·13	0·683	0·969	0·927	0·771
3·064	0·382	32·41	0·903	0·990	0·980	0·973	16·96	1·782	31·40	0·653	0·967	0·921	0·739
3·884	0·479	31·86	0·883	0·989	0·974	0·963	18·94	1·954	31·27	0·630	0·965	0·916	0·713
4·045	0·497	32·27	0·878	0·988	0·973	0·955	21·70	2·180	31·15	0·600	0·962	0·910	0·678
4·759	0·579	32·22	0·861	0·987	0·970	0·945	25·06	2·441	31·28	0·566	0·959	0·903	0·642
5·299	0·639	32·48	0·847	0·986	0·968	0·930	27·81	2·650	31·16	0·543	0·957	0·897	0·616
6·381	0·760	31·86	0·825	0·983	0·962	0·919	31·68	2·928	31·19	0·512	0·954	0·889	0·585
7·219	0·852	31·63	0·809	0·981	0·957	0·906	36·47	3·255	31·38	0·480	0·951	0·881	0·553
8·188	0·953	31·79	0·789	0·980	0·953	0·885							

p-*Dichlorobenzene solutions.*

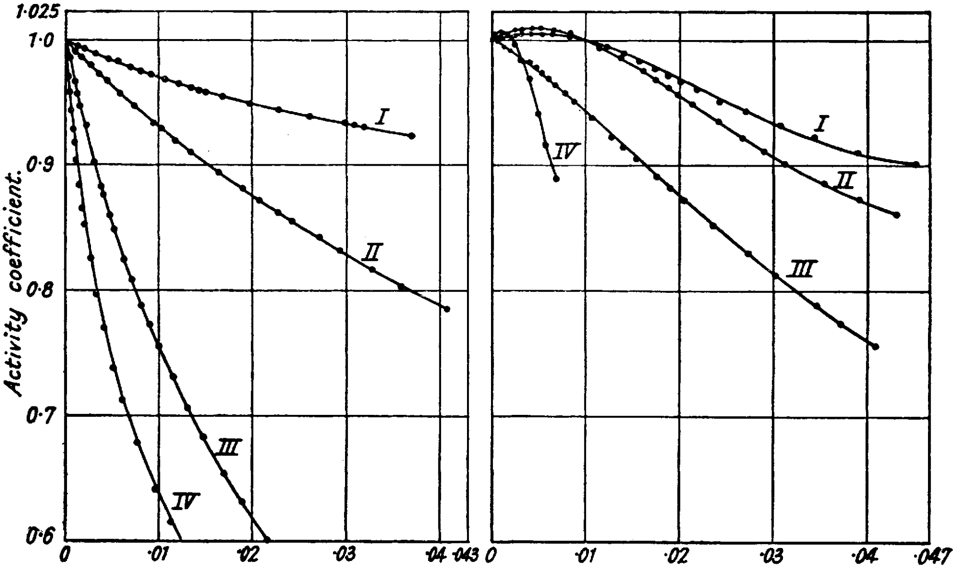
0·710	0·069	—	0·998	—	—	—	12·87	1·194	6·47	0·924	0·996	0·993	1·007
1·331	0·129	—	0·995	—	—	—	14·21	1·312	6·55	0·915	0·993	0·990	1·007
2·068	0·200	—	0·992	—	—	—	15·47	1·421	6·60	0·906	0·990	0·986	1·006
2·694	0·260	—	0·989	—	—	—	17·67	1·608	6·54	0·891	0·983	0·977	1·006
4·152	0·399	6·57	0·982	1·007	1·010	1·002	19·26	1·741	6·38	0·881	0·978	0·970	1·004
4·711	0·452	6·45	0·979	1·007	1·010	1·002	20·75	1·865	6·37	0·872	0·973	0·965	1·002
5·383	0·515	6·47	0·975	1·007	1·010	1·002	23·81	2·116	6·25	0·852	0·962	0·950	0·997
6·047	0·577	6·50	0·970	1·006	1·009	1·003	27·53	2·410	6·21	0·830	0·952	0·934	0·986
6·867	0·653	6·45	0·965	1·005	1·008	1·004	30·54	2·639	6·32	0·812	0·945	0·925	0·970
7·895	0·748	6·49	0·958	1·004	1·007	1·005	34·82	2·958	6·24	0·789	0·936	0·908	0·942
8·833	0·833	6·56	0·952	1·004	1·005	1·006	37·60	3·157	6·20	0·775	0·930	0·901	0·917
10·82	1·013	6·55	0·938	1·000	1·000	1·007	41·28	3·422	6·20	0·757	0·922	0·891	0·890

Average values of K_a: in benzene, 31·64; in *p*-dichlorobenzene, 6·42.

Heat of Formation of p-*Toluidine* o-*Tolyloxide*.—The average values of K_a (Table II) have been applied in the isochore (cf. this vol., p. 260); whence $Q = -6000$ cals., and the reaction is exothermic ($T_1 = 277{\cdot}4°$; $T_2 = 324{\cdot}7°$). This differs from the value ($Q = -6800$ cals.) previously found for pyridine and quinoline *o*-chlorophenoxides.

FIG. 2.

Molar ratio (M).



A. *Benzene solutions.* B. *Dichlorobenzene solutions.*

I, p-*Toluidine* (γ_A); II, o-*cresol* (γ_B); III, p-*toluidine and* o-*cresol together in solution* (γ); IV, p-*toluidine* o-*tolyloxide, undissociated* (γ_{AB}).

DISCUSSION OF RESULTS.

The values of K_a (Table II) are as consistent as, but much less than, those already reported (*loc. cit.*) for *o*-chlorophenoxides; evidently the tolyloxide is dissociated to a much greater extent than the chlorophenoxides. This accords with the views of Buehler, Hisey, and Wood (*J. Amer. Chem. Soc.*, 1930, **52**, 1939), who consider that such substitution of a methyl group for chlorine lowers the stability of molecular compounds.

As in earlier parts of this series, the solvent *p*-dichlorobenzene is again found to give dilute solutions in which the activity coefficients of single solutes exceed unity (Fig. 2, B). If *p*-dichlorobenzene exhibits dipole association (cf. Martin and George, J., 1933, 1413), this should virtually increase the molecular concentration of the solute and hence increase its activity. In more concentrated solutions, the dipole association of the solvent will be reduced by dilution and, simultaneously, the solute will tend to associate. Both of these effects should tend eventually to depress the activity coefficients of the solutes below unity (*e.g.*, Fig. 2, B, curve I).

As before (*loc. cit.*), γ_{AB} values (Fig. 2, curves IV) are markedly low. If undissociated compounds of the type AB are of the polar character previously suggested, their low activity in solution may then be due to strong dipole association (cf. Bury and Jenkins, this vol., p. 688).

The difference (800 cals.) between the heat of formation of *p*-toluidine *o*-tolyloxide and the *o*-chlorophenoxides is due to the different characters of *p*-toluidine and *o*-cresol compared with the bases and phenol previously used. As judged by ionisation constants (Landolt–Börnstein, "Tabellen," 1927), the bases quinoline, pyridine, and *p*-toluidine have the same character, but *o*-cresol and *o*-chlorophenol are very different. Therefore, there seems some justification for attributing the marked difference in heat of formation, now under discussion, to this dissimilarity of these phenols. In terms of the theory of Allan, Oxford, Robinson, and Smith (J., 1926, 402), this dissimilarity evidently means that the phenolic hydrogen in *o*-chlorophenol is more positive than that in *o*-cresol, and consequently the former hydrogen atom would tend to form a stronger co-ordination link with nitrogen (see this vol., p. 263). This would be expected to give a greater heat of formation for *o*-chlorophenoxides. Incidentally, if *o*-chlorophenol is chelated (Sidgwick and Callow, J., 1924, **125**, 527), it might be expected that energy absorbed in breaking down the chelate ring would reduce the exothermic heat of formation with a base, so that it is less than in the case of *o*-cresol (unchelated) and a base. That the respective heats of formation differ in the opposite sense may therefore be due to absence of chelation in *o*-chlorophenol.

Values for heats of formation of covalent links (*Ann. Reports*, 1931, **28**, 401) include N–H = — 90,000 cals., and this differs markedly from the heat of formation discussed here (*viz.*, — 6000 cals. approx.). If our assumption (*loc. cit.*) of a co-ordinate link $N \rightarrow H$ is correct, it would involve two co-ordinate electrons occupying a second quantum group in the hydrogen atom (Sidgwick, " The Covalent Link in Chemistry," 1933), and this should require less energy than the formation of a covalent link with electrons only in the first quantum group of the atom. von Elbe (*J. Chem. Physics*, 1934, **2**, 73) has calculated the heat of formation (—11,000 cals.) of dimeric *n*-alcohol molecules, which are thought to contain the group $O \rightarrow H$ (Sidgwick, *Z. Elektrochem.*, 1928, **34**, 450). On the other hand, the covalent link O–H has the value —110,000 cals. (*loc. cit.*). It thus appears that the heat of formation of a co-ordinate link involving hydrogen is only about 10% of that of the corresponding covalent link.

SUMMARY.

The true equilibrium constant, $K_a = a_{AB}/a_A a_B$, has been calculated for the dissociation of *p*-toluidine *o*-tolyloxide in benzene and in *p*-dichlorobenzene. Thus, two average values of K_a have been found for the two mean temperatures, $T_1 = 277{\cdot}4°$ and $T_2 = 324{\cdot}7°$, and the van 't Hoff isochore has been applied to calculate the heat of formation ($Q = -$ 6000 cals.) of the complex.

The difference between this value and that already reported (— 6800 cals.) for *o*-chlorophenoxides has been discussed, and an explanation suggested in terms of the general electronic effect of substituting CH_3 for Cl in phenols.

Heats of formation of covalent and co-ordinate links are discussed.

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