57. *The Nature of the Co-ordinate Link. Part V.** *The Equilibrium between* cis- *and* trans-*Bis(triethylphosphine)dichloroplatinum.*

By J. Chatt and R. G. Wilkins.

The isomerisation of *cis*-$(PEt_3)_2PtCl_2$ in benzene solution at 20—35° is an endothermic reaction, $\Delta H = 2470$ cal./mole, $\Delta G = -1480$ cal./mole, $\Delta S = 13{\cdot}3$ cal. mole^{-1} degree^{-1}. After allowance has been made for possibly greater association of benzene with the *cis*-isomer (to account for the entropy change) and a large liberation of energy owing to favourable spatial redistribution of electric charge when the highly polar *cis*- is converted into the non-polar *trans*-isomer, the *cis*-isomer is found to be more stable than the *trans* to the extent of about 10 000 cal. This represents the increase in bond energy when the phosphorus atoms are in *cis*- as compared with *trans*-configuration and gives strong support to the view that π-bonding through *d*-orbitals in the phosphorus and the platinum atoms plays a significant part in the binding.

In Part I of this series (*J.*, 1950, 2308) it was reported, on the basis of the crude measurements of the change in equilibrium position between *cis*- and *trans*-$(PPr^n_3)_2PtCl_2$ at 160° and 195°, that the heat content of the *trans*- is greater than that of the *cis*-isomer; nevertheless, the equilibrium mixture contained only 3·2% (at 25°) of *cis*-material, indicating a fairly large entropy difference between these two isomers. These observations are in marked contrast with the thermodynamic relation of geometric isomers in carbon chemistry, where entropy changes are almost zero and the heat content of the *cis*- is usually greater than that of the *trans*-isomer. A greater stability of the *cis*-isomer is to be expected if *d*-orbitals contribute in some special manner, probably by π-bonding, to the strength of the P–Pt bonds to a greater (or smaller) extent than to the Pt–Cl bonds (Chatt, *Nature*, 1950, **165**, 637; Chatt and Williams, *J.*, 1951, 3061). It was therefore important to make exact measurements of equilibria in this series of complexes.

Bis(triethylphosphine)dichloroplatinum was chosen for this study because the position of equilibrium is more favourable for exact measurement than in the propyl series. Also there is possible ambiguity regarding the true value of the equilibrium constant in the latter case because the equilibrium mixtures prepared from *cis*- and from *trans*-$(PPr_3)_2PtCl_2$ were not exactly identical. In the ethyl series this effect is so slight as to be negligible (see p. 277).

cis- and *trans*-$(PEt_3)_2PtCl_2$ do not isomerise spontaneously in solution at room temperature or in benzene at the boiling point, but isomerisation occurs rapidly in solution at room temperature in the presence of a trace of free triethylphosphine and spontaneously in ethyl alcohol at 100° (Cahours and Gal, *Compt. rend.*, 1870, **70**, 891). The equilibrium may be quenched by the addition of a trace of $(PEt_3)_2Pt_2Cl_4$, sufficient to react with all the free phosphine (cf. Chatt and Wilkins, *J.*, 1951, 2532). Separation of the isomers in the quenched equilibrium mixture by extraction of the *trans*- from the insoluble *cis*-isomer with ether is sufficiently accurate to give the approximate position of equilibrium. Samples of the pure *cis*- and the pure *trans*-isomer were isomerised in benzene at 25° and both isomers were separated quantitatively from the quenched equilibrium mixture, weighed, and identified by mixed melting points. Thus it was demonstrated that only these two isomers were present in the mixture; no side reactions were detectable, and the equilibrium concentrations of each isomer thus determined agreed, within the lower limits of accuracy of this method, with those found by the following less direct method.

The *cis*- has a large dipole moment (10·7 D) and the *trans*-isomer a zero moment (Jensen, *Z. anorg. Chem.*, 1936, **229**, 250). Thus we were able to determine accurately, by dielectric-constant measurement of benzene solutions, the equilibrium concentration of *cis*-isomer. The effects of the relatively large equilibrium concentration of *trans*-isomer and of the trace of triethylphosphine catalyst were both accurately allowed for.

---

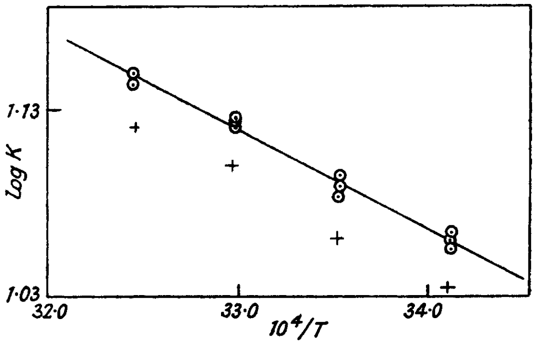
* Part IV, *J.*, **1951**, **3061**.

The reaction *cis*-$(PEt_3)_2PtCl_2 \rightleftharpoons$ *trans*-$(PEt_3)_2PtCl_2$ was investigated in benzene solution. Only 7·6% of *cis*- is present in equilibrium with its *trans*-isomer at 25°. The dielectric-constant method being used, the equilibrium constant (K), for this reaction was determined at different temperatures in the range 20—35° and less accurately at 45° and 60°. The relationship (see figure) :

$$\log K = 2{\cdot}901 - 540/T \quad (T = 293\text{—}308°\ \text{K})$$

was computed from these values by the method of least squares, and the following thermodynamic functions at 25° were obtained :

ΔH = heat absorbed in the reaction = 2470 ± 210 15°-cal.
ΔG = change in free energy = -1480 ± 12 cal.
ΔS = change in entropy = 13·3 ± 0·7 cal. mole^{-1} degree^{-1}.



○ *Equilibrium approached from* trans-*side.*
+ *Equilibrium approached from* cis-*side.*

These values contrast with those for the isomerism of geometrically isomeric hydrocarbons in the gaseous phase where the *cis* to *trans* change is usually slightly exothermic and ΔS almost zero (Table 1).

TABLE 1. *Values of* ΔH, ΔG *(cal./mole), and* ΔS *(cal. mole*$^{-1}$ *degree*$^{-1}$*) for the isomerisation of geometrically isomeric hydrocarbons,* cis *to* trans, *in the gas phase at* 25° (from " Selected Values of Properties of Hydrocarbons," Nat. Bur. Stand., Washington).

Hydrocarbon	ΔH	ΔG	ΔS
But-2-ene	−1040	− 731	−1·04
Pent-2-ene	− 880	− 598	−0·95
Hex-2-ene	−1000	− 720	−0·95
Hex-3-ene	−1000	− 800	−0·69
1 : 2-Dimethyl*cyclo*pentane	−1710	−1760	+0·16
1 : 3-Dimethyl*cyclo*pentane	− 540	− 540	0·00
1 : 2-Dimethyl*cyclo*hexane	−1870	−1610	−0·86
1 : 3-Dimethyl*cyclo*hexane	+1940	+1550	+1·38
1 : 4-Dimethyl*cyclo*hexane	−1900	−1490	−1·35
Compare also :			
Ethylene dibromide (gas, 150°) *	−130 ± 300	17 ± 40	−0·34 ± 0·8
Ethylene dichloride (gas, 185°) †	+ 723	+500	+0·49
Ethylene dichloride (in benzene, 150°) ‡	+1200	+750	+1·1

* Noyes and Dickinson, *J. Amer. Chem. Soc.*, 1943, **65**, 1427.
† Wood and Stevenson, *ibid.*, 1941, **63**, 1650.
‡ Wood and Dickinson, *ibid.*, 1939, **61**, 3259 (these values are not sufficiently accurate to be significantly different from those given for the gaseous phase).

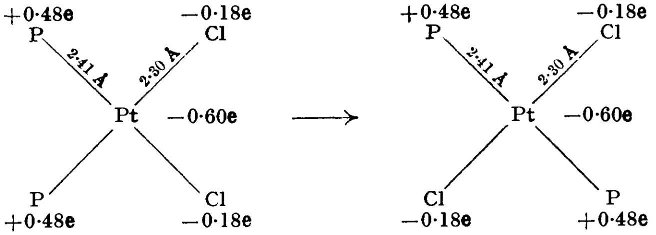
The comparatively large positive entropy change during the isomerisation of the *cis*-platinous complex is probably bound up with the large electric dipole moment which is neutralised during the isomerisation. The *cis*-complex is generally insoluble in non-polar or slightly polar solvents, *e.g.*, petroleum or diethyl ether, but dissolves slightly in benzene, possibly because the relatively flat, readily polarisable benzene molecules can associate with the flat molecule of the complex, and in the intense field of the dipole, become polar. When isomerisation occurs, the large dipole moment of the *cis*-complex is replaced by two smaller opposing moments; these will doubless cause some association of benzene, but smaller than that with the *cis*-isomer. The liberation of the excess of associated benzene would account for the large entropy change during the isomerisation

$$cis\text{-}(PEt_3)_2PtCl_2,nC_6H_6 \rightleftharpoons trans\text{-}(PEt_3)_2PtCl_2,mC_6H_6 + (n - m)C_6H_6$$

If we assume that the entropy of association of the benzene is of the same order as that of freezing benzene (8·55 cal. mole^{-1} degree^{-1}), then the order of $(n - m)$ is $13{\cdot}3/8{\cdot}55 = 1{\cdot}5$, which is reasonable and probably a minimum value.

The heat change during the isomerisation of the *cis*-isomer is made up of three important components: (1) The energy change during the discharge of the electric dipole; (2) the difference in heat of solution of the two isomers from an infinitely dilute gas phase into benzene solution at 25°; (3) the change in bond energy which occurs during isomerisation.

(1) To estimate the first, we know that the interatomic distances in complex compounds of similar types are given sufficiently accurately by the sum of the covalent radii (Mann and Wells, *J.*, 1938, 702), and that the dipole moment of *cis*-$(PEt_3)_2PtCl_2$ in benzene solution is $10{\cdot}7 \times 10^{-18}$ e.s.u. (Jensen, *loc. cit.*). If we assume the Pt–Cl bond moment to be 2×10^{-18} e.s.u., which is a reasonable value [cf. Jensen and Nygaard's value $2{\cdot}5 \times 10^{-18}$ e.s.u. for the Ni–Br bond (*Acta Chem. Scand.*, 1949, **3**, 474)], and also that the smaller PEt_3 moments may be neglected, then the change in the electrical state of the molecule on isomerisation can be represented as in the accompanying scheme.



Using these approximate representations, we calculate the energy dissipated when the *cis*- is converted into the much more favourable *trans*-arrangement to be equivalent to a heat of isomerisation of −15 000 cal./mole.

The charge of −0·60e on the platinum atoms is not in accordance with Pauling's postulate that the resultant electric charge on metal atoms tends to be zero (Contribution to the Study of Molecular Structure, Volume Commémoratif Victor Henri, p. 1, Maison Desoer, Liége, 1947—1948). If we assume it to be zero and attribute all the dipole moment of the *cis*-complex to charges on the phosphorus and chlorine atoms, then each phosphorus atom would have a charge of +0·38e and the chlorine atoms −0·38e. If it is assumed that the charges on these atoms are the same in the *trans*-complex, then the energy dissipated when the *cis*- is converted into the *trans*-complex would be 13 000 cal./mole.

From these two approximations it seems that the loss of electrical energy when the *cis*- is converted into the *trans*-isomer is of the order of 14 000 cal./mole.

We have used the dipole moment measured in benzene solution instead of in the gaseous phase, and assumed the P–Pt–P angle in the *cis*-compound to be 90°, although the repulsion of charges on the phosphorus atoms would make it slightly larger. These will have little effect on the order of the calculated figure, and are compensating errors.

(2) In benzene solution we also have, associated with the *cis*-isomer, the heat of association of the $(n - m)$ molecules of benzene and any heat due to dipole association. Whatever the cause of the observed entropy change of 13·3, the heat associated with it cannot be greater than $13{\cdot}3T = 4000$ cal., which is probably a fair estimate of the maximum value of the second component listed above.

(3) Factors (1) and (2) together would account for a heat of isomerisation of about −10 000 cal. The difference between this and the observed +2500 cal. (*i.e.*, 12 500 cal.)

is thus an approximation to item (3), the difference in total bond energy of the two isomers. We have no means of assessing the error in the figure derived from the above approximations, but even if the electrical energy is wrongly assessed by 50% or 7000 cal., which seems an exaggerated error, the total bond energy of the *cis-* is still higher than that of the *trans*-isomer by at least 5000 cal. and the difference is more probably of the order of 10 000 cal.

All the bonds in both *cis-* and *trans*-isomers are the same, and only the configuration round the platinum atom has changed. Therefore, the large increase in bond energy on converting the *trans-* into the *cis*-complex must arise from placing the phosphorus atoms in *cis*-positions to each other. If *d*-orbitals in the phosphorus and platinum atoms play a part in the binding by π-bonding, then in the *cis*-isomer each phosphorus atom can be bound by a different *d*-orbital in the platinum atom, whereas in the *trans*-isomer each phosphorus atom is competing for the same *d*-orbitals, leading to weaker binding. It follows also that the part played by *d*-orbitals in binding chlorine to platinum must be very different from that in the binding of phosphorus, otherwise placing the chlorine atoms in *trans*-positions to the phosphorus atoms instead of *trans*-position to each other would have led to no increase in bond energy. This correlates with the position of chlorine, which is much lower than phosphorus, in the *trans*-influence series (see Chatt and Williams, *loc. cit.*).

No previous quantitative isomerisation studies of platinous complexes are recorded, but Nikolaev (*Compt. rend. Acad. Sci. U.R.S.S.*, 1938, **20**, 571) noted by plotting heating curves that the isomerisation of solid *cis*-$(NH_3)_2PtCl_2$ is exothermic. *d*-Electrons from the platinum atom can take no part in binding platinum to nitrogen because no 2*d* or other vacant orbitals are available to receive them in the nitrogen atom. From our above study and the *trans*-influence series, *d*-electrons play only a minor part in the binding of chlorine, as compared with phosphorus, to platinum, so we should expect that little energy would be lost by placing the chlorine atoms *trans* to each other. Thus the exothermal change is to be expected in the isomerisation of the *cis*-diammine. However, as the lattice forces are probably much greater in the crystals of the highly polar *cis*-diammine than in its *trans*-isomer, these qualitative measurements are not strictly comparable to our own, which were made in solution. It would be interesting to make isomerisation studies in solution of $(NEt_3)_2PtCl_2$ if such compounds could be prepared, because then we would get some direct measure of the energy to be gained by taking the chlorine atoms from the *trans-* to the *cis*-positions with respect to each other, free from interference by the *trans*-groups.

This study also serves to emphasise the importance of the entropy term in determining the position of equilibrium in reactions involving the formation or destruction of highly polar molecules, and how completely erroneous conclusions regarding relative stability can be arrived at by consideration of only equilibrium positions or decomposition temperatures in the field of co-ordination chemistry.

We are continuing these isomerisation studies to see how different hydrocarbon radicals, acid radicals, and Group V (and VI) elements affect the equilibrium in complexes analogous to $(PEt_3)_2PtCl_2$. Our preliminary survey of the field, so far as platinous complexes are concerned, is summarised in Part III (*J.*, 1951, 2532).

EXPERIMENTAL

cis- and *trans*-Bis(triethylphosphine)dichloroplatinums were prepared like their tri-*n*-propyl homologues (Chatt and Wilkins, *loc. cit.*); they had m. p. 192—193° and 142—143° respectively [Jensen (*Z. anorg. Chem.*, 1936, **229**, 238) gives 191—192° and 142—143°].

Examination of the Isomerisation of cis- *and* trans-$(PEt_3)_2PtCl_2$, *by Separation, Identification, and Weighing of the Products.*—Each pure isomer, in benzene (50 c.c.), was isomerised at 25° by addition of triethylphosphine (0·5 c.c. of M/30-solution). After 30 minutes the equilibrium had been established and was quenched by addition of $(PEt_3)_2Pt_2Cl_4$, sufficient to react with all the free phosphine. This produced mainly a small extra quantity of *trans*-$(PEt_3)_2PtCl_2$, for which allowance was made. The benzene was now evaporated at 15 mm., and the last traces were removed at 0·05 mm. pressure. The pale yellow *trans*-isomer was extracted with ether and decanted from the residue; extraction was repeated until the washings were colourless. The white residue of *cis*-isomer was thoroughly dried at 0·05 mm. pressure and weighed in its tared container, from which it was removed by washing with acetone. The *trans*-isomer was similarly obtained from its ethereal solution and weighed. The two isomers were then recovered by complete evaporation of the acetone solutions and after drying at 0·05 mm. had the m. p.s, alone and mixed with an authentic specimen, given in Table 2.

TABLE 2.

Wt. of starting material, mg.	Wt. of PEt_3, catalyst, mg.	Wt. of $(PEt_3)_2Pt_2Cl_4$ added to remove catalyst, mg.	Materials recovered from equilibrium mixture : *cis*-compound,			*trans*-compound,			
			mg.	m.p.	mixed mp.	mg.	m.p.	mixed m.p.	*K*
	2·0	8·0	0·6	—	—	9·0	—	—	—
cis, 301·0	2·0	9·9	22·6	187—188°	188—189°	292·6	140·5—141·5°	141·5—142·5°	12·9
trans, 306·9	2·0	9·8	22·0	188—189	188·5—189·5	301·8	140·5—141·5	141·5—142·5	13·7
cis, 501·6	1·8	7·1	42·3	186—187	—	473·6	139—140	—	11·2
trans, 507·9	1·8	7·1	42·3	187—188	—	477·6	140—141	—	11·3

Preparation of Dichlorobis(triethylphosphine)-μμ′-dichlorodiplatinum, $(PEt_3)_2Pt_2Cl_4$.—This compound was prepared by heating crude $(PEt_3)_2PtCl_2$ with $PtCl_2$ to 187° for 5 minutes at which temperature considerable blackening occurred (Chatt, *J.*, 1950, 2306); recrystallised from acetone, the orange-yellow *compound* had m. p. 223—224° (Found: C, 18·7; H, 4·0. $C_{12}H_{30}Cl_4P_2Pt_2$ requires C, 18·7; H, 3·9%).

Determination of the Equilibrium Constant (K) *of the Isomerisation Reaction in Benzene Solution.*—*cis*-$(PEt_3)_2PtCl_2$ in benzene solution raises the dielectric constant above that of benzene by about 70 times as much as an equal quantity of the *trans*-isomer. We could thus determine accurately the quantity of *cis*-isomer in presence of its relatively large equilibrium quantity of *trans*-isomer by determining the increase in capacity of an electrical condenser, or cell, when the benzene dielectric, which also contained the catalytic PEt_3, was replaced by the solution under test, in which the total weight of the mixed isomers was known.

The cell used to make these measurements was identical with that of Jenkins and Sutton (*J.*, 1935, 609) except that it was rhodium-plated internally. The changes in capacity of the cell were measured by a heterodyne capacity meter based on that of Hill and Sutton (see *J.*, 1949, 2313). Our standard variable condenser was a Sullivan micrometer condenser of range 5—13 μμF.

The quantities of benzene used in these experiments were those delivered from one particular 50-c.c. graduated flask at the temperature of the determinations, which were at 15°, 43·81 g.; 20°, 43·58 g.; 25°, 43·36 g.; 30°, 43·14 g.; 35°, 42·94 g.

Over the range of concentrations used in these experiments the increase in capacity (ΔC) of the cell, over that with pure benzene as dielectric, was directly proportional to the quantity of added material. At a given temperature when the cell contained a solution of the equilibrium mixture:

$$\Delta C = k_c W_c + k_t W_t + k_p W_p$$

where W_c = weight of *cis*-isomer, W_t = weight of *trans*-isomer, W_p = weight of triethylphosphine present as catalyst, all in the standard quantity of benzene appropriate to the temperature of the determination. At each temperature k_c was determined by making up solutions with W_t and W_p zero, and k_t similarly. As a further check, mixtures of *cis*- and *trans*-isomers were made up and shown to obey the above relationship. Also the addition to the equilibrium mixture of a further quantity of triethylphosphine, equal to that normally used to catalyse the isomerisation, produced exactly the same change in ΔC as when it was added to pure benzene. Thus, to the accuracy of our measurements and at the low concentrations used, the phosphine exists in presence of the platinous complexes in the free state and not as the salt $[(PEt_3)_3PtCl]Cl$ (cf. Nyholm, *J.*, 1950, 848).

To determine the equilibrium constant, a weighed quantity (W) of the appropriate isomer was dissolved in the standard quantity of benzene, containing a trace of triethylphosphine, at the temperature of the determination and transferred to the cell contained in a thermostat. The capacity of the cell changed rapidly until isomerisation was complete (*ca.* 5—20 minutes, depending on the quantity of added phosphine and the temperature). The difference between the final steady capacity and the capacity with the standard volume of benzene containing the small quantity of phosphine catalyst only, at the same temperature is $\Delta C - k_pW_p$; K was calculated from the equations :

$$\Delta C - k_pW_p = k_cW_c + k_tW_t ; \quad W = W_c + W_t ; \quad K = W_t/W_c$$

Because of the inconveniently low solubility of *cis*-$(PEt_3)_2PtCl_2$, most determinations were made by isomerisation of a solution of the very soluble *trans*-isomer, but one sample of *cis*-isomer was isomerised at each temperature. Temperatures were measured with a standardised mercury-in-glass thermometer with accuracy limits ±0·02°. The results are recorded in the following tables.

Values of k_c *and* k_t.

Temp.	W_c, g.	ΔC, μμF	k_c	W_t, g.	ΔC, μμF	k_t
19·85°	0·0366	0·993	27·1	0·4004	0·158	0·395
	0·0396	1·050	26·5	0·5007	0·201	0·401
	0·0431	1·149	26·7			
			(mean 26·8)			(mean 0·398)
24·97	0·0418	1·112	26·6	0·6090	0·231	0·379
	0·0426	1·129	26·5			
	0·0521	1·376	26·4			
	0·0540	1·436	26·6			
			(mean 26·5)			
30·00	0·0390	0·997	25·6	0·5090	0·215	0·422
	0·0420	1·076	25·6	0·6125	0·244	0·398
			(mean 25·6)			(mean 0·410)
35·01	0·0453	1·122	24·8	0·4936	0·198	0·401
	0·0457	1·135	24·8	0·5935	0·231	0·389
	0·0485	1·195	24·6			
			(mean 24·7)			(mean 0·395)

Temp., ° K.	$10^4/T$	W, g.	W_p, g.	$\Delta C - k_pW_p$, μμF	W_c, g.	W_t, g.	K	log K
Isomerisation of trans-$(PEt_3)_2PtCl_2$.								
293·00	34·13	0·4455	0·0020	1·125	0·0359	0·4096	11·4	1·057
		0·4939	0·0020	1·254	0·0401	0·4538	11·3	1·054
		0·5023	0·0020	1·261	0·0402	0·4621	11·5	1·061
298·12	33·54	0·4369	0·0018	1·020	0·0327	0·4042	12·35	1·092
		0·5079	0·0018	1·198	0·0385	0·4694	12·2	1·086
		0·6090	0·0018	1·452	0·0468	0·5622	12·0	1·080
303·15	32·99	0·5090	0·0013	1·109	0·0357	0·4733	13·25	1·123
		0·6003	0·0018	1·314	0·0424	0·5579	13·15	1·119
		0·6125	0·0013	1·333	0·0429	0·5696	13·3	1·123
308·16	32·45	0·4936	0·0009	0·990	0·0327	0·4609	14·1	1·149
		0·5935	0·0009	1·205	0·0399	0·5536	13·9	1·142
Isomerisation of cis-$(PEt_3)_2PtCl_2$.								
293·00	34·13	0·5980	0·0018	1·584	0·0510	0·5470	10·7	1·031
298·12	33·54	0·5016	0·0018	1·238	0·0401	0·4615	11·5	1·061
303·15	32·99	0·5980	0·0018	1·349	0·0438	0·5542	12·6	1·100
308·16	32·45	0·5980	0·0018	1·257	0·0420	0·5560	13·2	1·121

The equilibrium constants at 45° and 60° were determined slightly less accurately by quenching the equilibrium by addition of $(PEt_3)_2Pt_2Cl_4$ and then allowing the mixture to cool to 25° before putting it in the cell. The values of K thus obtained were at 45°, 16·2, and at 60°, 21·2, from the *trans*-side only.

It is to be noted that the equilibrium position is slightly different when approached from the *cis*- as compared with the *trans*-side. The tripropyl complexes show the same effect to a marked extent and in a peculiar manner which will be described in a subsequent communication. As the result of an extensive study of the propyl derivatives, we are convinced that the more accurate value is that obtained by isomerisation of the *trans*-complex. However, even if the values derived from isomerisation of the *cis*-triethylphosphine complex were correct, then the values of $\Delta H = 2470$ cal., $\Delta G = 1395$ cal., and $\Delta S = 13{\cdot}0$ cal. mole^{-1} degree^{-1} derived on this assumption are essentially the same as those quoted, although outside the experimental error. They invalidate in no way the arguments contained in the theoretical part of this communication.

The authors are greatly indebted to Dr. H. Kolsky and Dr. A. R. Miller for valuable discussions, to Mr. D. J. Odds for experimental assistance, and to Miss B. E. Walker for help in carrying out the computations.

IMPERIAL CHEMICAL INDUSTRIES LIMITED, RESEARCH DEPARTMENT,
BUTTERWICK RESEARCH LABORATORIES,
THE FRYTHE, WELWYN, HERTS.

[*Received, August* 29*th*, 1951.]