Competitive Alkali-metal Flame Reactions. Part 5.[†] Reactions of Potassium Atoms with Fluorobenzene, Fluoroanisoles, and t-Butyl Chloride and of Potassium and Caesium Atoms with *p*-Alkylchlorobenzenes

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The kinetics of the abstraction of fluorine atom from fluorobenzene and fluoroanisoles by potassium atom and of chlorine atom from *p*-alkylchlorobenzenes by potassium and caesium atoms have been studied in the gas phase by a competitive method using t-butyl chloride and ethyl iodide as standards, respectively, in a modified diffusion flame reaction system. The results show that (a) the trend in the reactivities of fluorobenzene and fluoroanisoles follows the sequence $o > m > p >$ u, where *o*, *m*, *p*, and u mean *ortho-*, *meta-*, and *para*-substituted and unsubstituted fluorobenzene, respectively; (b) the sequence in the reactivities of *p*-alkylchlorobenzenes towards potassium and caesium atoms is *p*-t-butylchlorobenzene > *p*-chlorocumene > *p*-ethylchlorobenzene > *p*-chlorotoluene > chlorobenzene; and (c) the rate of abstraction of chlorine atom by caesium atom is faster than that by potassium atom.

THE abstraction of halogen atoms by alkali-metal atoms from halogenated compounds has been studied by many workers using various techniques, some of which allowed absolute kinetic parameters to be determined at one temperature.[1–4] With the modification of the diffusion flame technique [5] which provided for competitive reactions, using a halogenated substance as standard, it was possible to obtain relative rates and Arrhenius parameters.[5,6] Though the errors for such measurements were sometimes considerable and of an order of magnitude, the results nevertheless gave the expected trends in the reactivities of related substances.

Riding *et al.*[7] studied the abstraction of halogen atoms from substituted halogeno-benzenes and -pyridines by sodium atoms. They observed two types of trend in the rates, depending on the nature of the substituents, *i.e.* whether (a) the substituent was a single atom or (b) it was a group of atoms containing multiple bonds. For substituents which were single atoms, the trend followed the order $o > m > p >$ unsubstituted (u); for substituents which were groups of atoms the order was $o > p > m >$ u. The former trend was explained in terms of a negative group effect in which the substituent was normally electronegative. This resulted in the formation of a resonance structure in the transition state, leading to a lowering of the activation energy. The formation of resonance structures varied with the distance of the substituent from the halogen atom. Recently, Gowenlock *et al.*[2,4] used this polar effect to explain the gradation in the series of abstraction of chlorine atom by sodium atom from chloroalkyl-substituted hydrocarbons, silanes, and germanes.

The reactions involving groups of atoms as substituents were explained in terms of a complex stabilisation effect by the π-bonds of the substituent or the interaction of the lone pair of electrons of one of the atoms of the group through delocalisation of the pair by interaction with the π-electrons of the benzene ring.

Eyring and Smith [8] have also shown that the rate of abstraction depends, among other factors, on the net charge on the halogen atom which determined the rate of transfer of an electron from the sodium atom to the halogen atom. The greater the negative charge, the more difficult the transfer of the electron.

In view of these previous conclusions on the factors affecting the rate constant for the abstraction of halogen atom from halogen compounds by alkali-metals, an attempt is made in this work to investigate further inductive and hyperconjugative effects on the abstraction reaction.

EXPERIMENTAL

Apparatus and Procedure.—The apparatus and procedure used in this work are similar to those described previously.[3,5,6] The temperature of the reaction vessel was measured with a chromel–alumel thermocouple (± 0.2 K).

Analysis of Mixtures of Chlorides and Fluorides.—Potassium chloride and potassium fluoride are the solid products of abstraction by potassium atoms from t-butyl chloride and the fluorides, respectively. These substances were dissolved in water and their total concentration determined by conductometric titration using standard silver nitrate solution and platinum electrodes. The concentration of potassium fluoride was determined by titration of the solution with standard thorium nitrate [9] solution. The concentration of the chloride was then obtained by difference.

Analysis of Mixtures of Chlorides and Iodides.—The concentrations of the chloride and iodide products in the mixture were determined as described by Emovon and Ojo.[6]

Materials.—*t-Butyl chloride.* This was obtained from B.D.H. and fractionated. The fraction boiling between 322.7 and 323.7 K at 743.8 mmHg was used. The purity was determined by g.l.c. to be 98.6% and had $n_D^{21.5}$ 1.3858. (lit.,[10] b.p. 325.2 K at 760 mmHg; $n_D^{20.0}$ 1.3857).

Fluorobenzene. This was a B.D.H. product and was fractionated and the middle fraction boiling at 358.2 K and 743.8 mmHg and having $n_D^{21.55}$ 1.4682 was used (lit.,[10] b.p. 355.7 K at 760.0 mmHg; n_D^{20} 1.4677).

Fluoroanisoles. The fluoroanisoles were obtained from Fluka and fractionated. The middle fractions with the following physical constants were used: *p*-fluoroanisole, b.p. 427.2 K at 748.5 mmHg; $n_D^{21.5}$ 1.4882 (lit.,[11] b.p. 427.2 K at 760.0 mmHg; $n_D^{18.0}$ 1.4886); *m*-fluoroanisole, b.p. 429.2 K at 747.5 mmHg; $n_D^{21.5}$ 1.5061 (lit.,[10] b.p. 320.2 K at 12.0 mmHg); *o*-fluoroanisole, b.p. 427.2 K at

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754.0 mmHg; $n_D^{21.5}$ 1.4988 (lit.,[11] b.p. 427.2—428.2 K at 760.0 mmHg; $n_D^{17.5}$ 1.4969).

Ethyl iodide. This was obtained from B.D.H. and fractionated. The middle portion boiling in the range 343.2—344.2 K at 748.5 mmHg and having n_D^{20} 1.5280 was used.

p-*Chloro(ethyl)benzene*. This was prepared from chlorobenzene *via* *p*-chloroacetophenone obtained by acylation using redistilled acetic anhydride and anhydrous aluminium chloride in carbon disulphide.[12] Chloroacetophenone was subsequently reduced by the Huang-Minlon modification of the Wolf–Kishner reduction.[12] It was dried over calcium chloride and fractionated. The fraction boiling at 455.2 K and 746.0 mmHg and having $n_D^{21.5}$ 1.5182 was used after ascertaining its purity by g.l.c. (lit.,[11] b.p. 457.6 K at 760.0 mmHg; $n_D^{20.0}$ 1.5175).

p-*Chlorocumene*. This was prepared by the alkylation of chlorobenzene with isopropyl alcohol using boron trifluoride as catalyst.[13] The fraction boiling at 471.2 K was used.

p-*t-Butylchlorobenzene*. This was prepared by a Friedel–Crafts t-butylation reaction [14] and distilled. It had b.p. 483.2—484.2 K at 756.0 mmHg; $n_D^{21.5}$ 1.5128. The compound was found to be 98.2% pure by g.l.c.

Potassium. This was obtained from B.D.H. in jars under paraffin oil. Samples were freshly cut and transferred into freshly distilled xylene.

Caesium. This was obtained from Fluka in 1 g ampoules. The ampoules were broken under dry cyclohexene for use.

Nitrogen used as carrier gas was freed of oxygen by scrubbing it through Fiesers' solution and drying it over concentrated H_2SO_4. It was subsequently passed over heated sodium metal before use.

RESULTS

The reaction is represented by equations (1) and (2). From equation (1), $-d[RX]/dt = k_2[RX][K] = r_1$; from

$$RX + K \longrightarrow R\cdot + KX \qquad (1)$$

$$R'X' + K \longrightarrow R'\cdot + KX' \qquad (2)$$

equation (2), $-d[R'X']/dt = k_2[R'X'][K] = r_2$. Thus equation (3) applies assuming that r_1 and r_2 are proportional

$$\frac{r_1}{r_2} = \frac{k_2[RX][K]}{k_2'[R'X'][K]} = \frac{[KX]}{[KX']} \qquad (3)$$

to the amounts of potassium halides formed respectively. This leads to equation (4). The ratio of the bimolecular

$$\frac{k_2}{k_2'} = \frac{[R'X']}{[RX]} \cdot \frac{[KX]}{[KX']} \qquad (4)$$

rate constants for each pair of the reactants was obtained at various temperatures. Blank runs without alkali metal but with mixtures of t-butyl chloride and each of fluorobenzene and the fluoroanisoles showed neither chloride nor fluoride ions resulting from thermal decomposition of the compound throughout the range of temperature. Similarly, no chloride and iodide ions were obtained from mixtures of ethyl iodide and the alkylchlorobenzenes at the temperatures of the reactions. Also the titration of water suspensions of these compounds showed no evidence of hydrolysis.

The reactions studied were (5)—(17).

The reactions of the radicals resulting from the reactions represented in equations (1)—(17) were not investigated. However the peaks other than those for the reactant materials in the chromatograms indicate that these radicals underwent further reactions.

The relative bimolecular rate constants (k_2/k_2') were obtained from equation (4) and these were used to produce the

$$\text{t-}C_4H_9Cl + K \longrightarrow \text{t-}C_4H_9 + KCl \qquad (5)$$

$$C_6H_5 + K \longrightarrow C_6H_5 + KF \qquad (6)$$

$$p\text{-}MeOC_6H_4F + K \longrightarrow p\text{-}MeOC_6H_4 + KF \qquad (7)$$

$$m\text{-}MeOC_6H_4F + K \longrightarrow m\text{-}MeOC_6H_4 + KF \qquad (8)$$

$$o\text{-}MeOC_6H_4F + K \longrightarrow o\text{-}MeOC_6H_4 + KF \qquad (9)$$

$$C_2H_5I + K \longrightarrow C_2H_5 + KI \qquad (10)$$

$$C_2H_5I + Cs \longrightarrow C_2H_5 + CsI \qquad (11)$$

$$p\text{-}C_8H_{10}Cl + K \longrightarrow p\text{-}C_8H_{10} + KCl \qquad (12)$$

$$p\text{-}C_8H_{10}Cl + Cs \longrightarrow p\text{-}C_8H_{10} + CsCl \qquad (13)$$

$$p\text{-}C_9H_{12}Cl + K \longrightarrow p\text{-}C_9H_{12} + KCl \qquad (14)$$

$$p\text{-}C_9H_{12}Cl + Cs \longrightarrow p\text{-}C_9H_{12} + CsCl \qquad (15)$$

$$p\text{-}C_{10}H_{14}Cl + K \longrightarrow p\text{-}C_{10}H_{14} + KCl \qquad (16)$$

$$p\text{-}C_{10}H_{14}Cl + Cs \longrightarrow p\text{-}C_{10}H_{14} + CsCl \qquad (17)$$

Arrhenius plots shown in Figures 1—3. The relative Arrhenius parameters were calculated by the least squares method and are shown in Tables 1—3.

The absolute activation energy for the reactions investigated have been obtained by assuming that the reaction of alkali-metal atoms with methyl iodide has zero activation energy. The results of the relative rate constants at 523.2 K are shown in Tables 4—6.

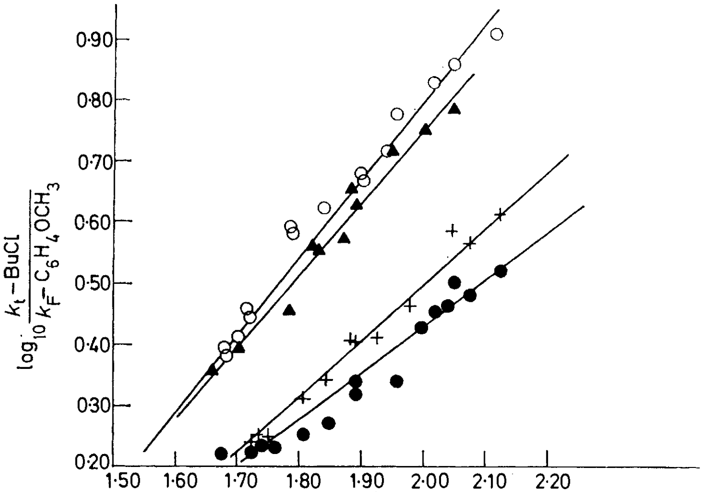


FIGURE 1 Arrhenius plots for reaction of potassium with: ○, fluorobenzene; ▲, *p*-fluoroanisole; +, *m*-fluoroanisole; ●, *o*-fluoroanisole

TABLE 1

Reactions of potassium atoms with mixtures of t-butyl chloride and each of fluorobenzene and fluoroanisoles

Reactant 1	Reactant 2	T/K	$E_2 - E_1$/ kJ mol^{1}	A_1/A_2
t-C_4H_9Cl	C_6H_5F	472.0—595.0	23.13 ± 1.01	0.024 ± 0.02
t-C_4H_9Cl	*p*-$MeOC_6H_4F$	487.7—603.2	22.33 ± 1.21	0.026 ± 0.02
t-C_4H_9Cl	*m*-$MeOC_6H_4F$	470.7—599.2	18.64 ± 0.59	0.036 ± 0.01
t-C_4H_9Cl	*o*-$MeOC_6H_4F$	468.7—598.7	15.72 ± 0.54	0.06 ± 0.01

TABLE 2

Reactions of potassium atoms with ethyl iodide and each of the *p*-alkylchlorobenzenes

Reactant 1	Reactant 2	T/K	$E_1 - E_2$/ kJ mol^{-1}	A_1/A_2
C_2H_5I	*p*-$C_8H_{10}Cl$	472.1—599.5	12.97 ± 0.08	1.83 ± 0.00
C_2H_5I	*p*-$C_9H_{12}Cl$	472.1—601.0	10.15 ± 0.17	2.62 ± 0.00
C_2H_5I	*p*-$C_{10}H_{14}Cl$	471.0—601.5	7.75 ± 0.08	2.89 ± 0.00

TABLE 3

Reactions of caesium atoms with ethyl iodide and each of the *p*-alkylchlorobenzenes

Reactant 1	Reactant 2	T/K	$E_1 - E_2$/ kJ mol^{-1}	A_1/A_2
C_2H_5I	*p*-$C_8H_{10}Cl$	470.5—602.0	11.01 ± 0.30	1.81 ± 0.01
C_2H_5I	*p*-$C_9H_{12}Cl$	470.0—603.2	9.19 ± 0.18	2.36 ± 0.00
C_2H_5I	*p*-$C_{10}H_{14}Cl$	468.0—603.2	6.45 ± 0.26	2.96 ± 0.01

TABLE 4

Relative rates for the reactions of potassium atoms with fluorobenzene and fluoroanisoles

Compound	E_a/kJ mol^{-1}	$\frac{k_{\text{compound}}}{k_{\text{fluorobenzene}}}$	$\frac{A_{\text{compound}}}{A_{\text{fluorobenzene}}}$
Fluorobenzene	35.38	1.00	1.00
p-Fluoroanisole	34.59	1.08	0.93
m-Fluoroanisole	30.90	1.87	0.67
o-Fluoroanisole	28.00	2.11	0.40

TABLE 5

Relative rates for the reactions of potassium atoms with *p*-alkylchlorobenzenes

Compound	E_a/kJ mol^{-1}	$\frac{k_{\text{compound}}}{k_{\text{chlorobenzene}}}$	$\frac{A_{\text{compound}}}{A_{\text{chlorobenzene}}}$
Chlorobenzene [6]	34.43	1.00	1.00
p-Chlorotoluene [6]	32.64	1.20	0.88
p-Ethylchlorobenzene	32.08	1.40	0.83
p-Chlorocumene	29.46	1.79	0.59
p-t-Butylchlorobenzene	26.86	2.81	0.62

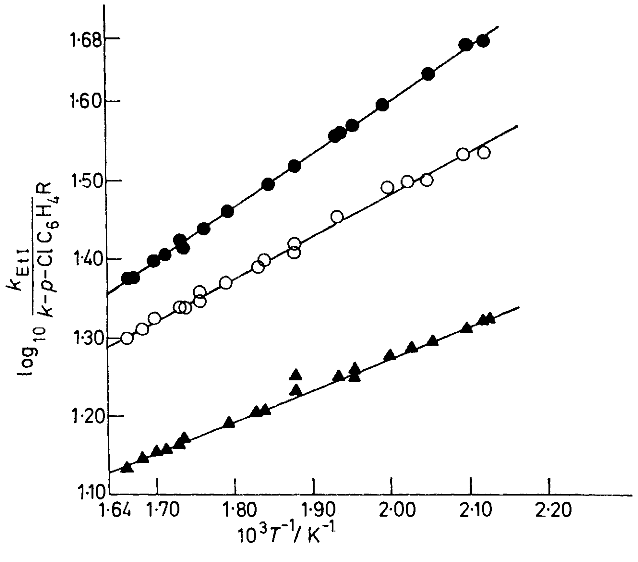


FIGURE 2 Arrhenius plots for reaction of potassium with: ●, *p*-chloroethylbenzene; ○, *p*-chlorocumene; ▲, *p*-chloro-t-butylbenzene

TABLE 6

Relative rates for the reactions of caesium atoms with *p*-alkylchlorobenzenes

Compound	E_a/ kJ mol^{-1}	$\frac{k_{\text{compound}}}{k_{p\text{-ethylchlorobenzene}}}$	$\frac{A_{\text{compound}}}{A_{p\text{-ethylchlorobenzene}}}$
p-Ethylchlorobenzene	23.28	1.00	1.00
p-Chlorocumene	21.46	1.17	1.77
p-t-Butylchlorobenzene	18.72	1.74	0.61

DISCUSSION

Eyring and Smith [8] showed that the inductive effect is a factor that influences the rate of abstraction of halogen atoms from organic halides by alkali-metals. The methoxy group has a $-I$ effect and therefore depending on its distance from the reaction centre can, to varying degrees, decrease the electron density at all positions in the ring. It thus facilitates the transfer of electron from the alkali-metal to the halogen atom, and the rate of abstraction will follow the order $o > m > p > u$ as shown in Table 4.

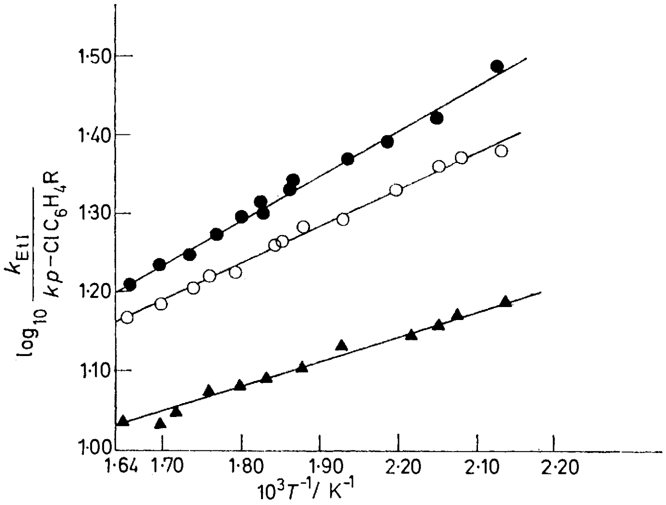
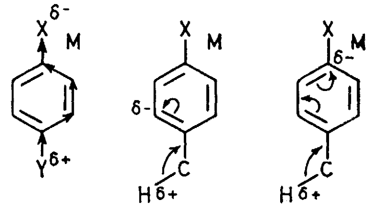


FIGURE 3 Arrhenius plots for reaction of caesium with: *p*-chloroethylbenzene; ○, *p*-chlorocumene; ▲, *p*-chloro-t-butylbenzene

The relatively unreactive alkyl substituents in the monosubstituted alkylchlorobenzene with a $+I$ effect have a relatively negligible effect on the C–Cl bond [2] but can contribute to the rate of abstraction of chlorine atom through inductive and hyperconjugative mechanisms. From the *para*-position, the increase in electron density at the reaction centre by the inductive effect of the alkyl groups follows the sequence $CH_3 < CH_3CH_2 < (CH_3)_2CH < (CH_3)_3C$.[15] This effect on the rate of reaction is contrary to the observed sequence which is *p*-t-butylchlorobenzene > *p*-chlorocumene > *p*-ethylchlorobenzene > chlorobenzene shown in Tables 5 and 6.

In hyperconjugation, there is a weak overlap of the π-electron system of the benzene ring with the molecular orbitals of the substituent alkyl group and the degree of this follows the sequence $CH_3 > CH_3CH_2 > (CH_3)_2CH > (CH_3)_3$. This effect will result in an increase in the electron density at the reaction centre, thus inhibiting this transfer of electron from the alkali-metal atom. Consequently the rate of abstraction would follow the reverse trend to the observed sequence. These effects are represented in the Scheme.

The reaction path for the abstraction as defined by Evans and Polanyi[15] does not explain the results obtained for simple molecules and one alternative reaction path may be considered. Evans *et al.*[15] described the path as the transfer of valence electron of the alkali-metal at a distance equivalent to the halogen–alkali-metal ion pair to the homolytically bound halogen atom along the C–X bond.[2] The halogen atom then breaks off as halogen ion from the organic residue to form alkali-metal halide.



SCHEME

The ease of acceptance of the electron depends on such other factors as the polarisability of the valence shell of the halogen atom. Trotman-Dickenson *et al.*[5] proposed a circular approach of the alkali-metal atom to the halogen atom in order to account for the observed *A* factors. This picture would for a given halogen atom suggest a decrease in the reactivity in the order $(CH_3)_3C < (CH_3)_2CH < CH_3CH_2 < CH_3$. Apart from the explanation from the methoxy group based on the inductive effect, the experimental results give a contrary trend. However, in the methoxy substituent, delocalisation of the electron pair on the oxygen atom into the ring would increase electron density in the *ortho*- and *para*-positions leaving the *meta*-position only slightly affected. On this basis, the rate sequence would be $o > m > p > \mathrm{u}$. This sequence has not been obtained in this work. Consequently we propose that the electron from the alkali-metal atom is transferred into the π-electron system of the benzene ring at the α-carbon atom of the halide and this acts as the driving force promoting the heterolysis[16] of the α-C–Cl bond. Such a transfer of electron from sodium atom to carbon atom would explain the general trend obtained in this work.

Ogg and Polanyi[17] suggested from the potential energy diagrams for the abstraction of halogen from halogen compounds by alkali-metal atom that the rates follow the sequence $\mathrm{Li} < \mathrm{Na} < \mathrm{K} < \mathrm{Rb} < \mathrm{Cs}$. Assuming that the *A* factors for the abstraction of chlorine atom from the chloro compound by both potassium and caesium atoms are essentially the same, the rates may be determined by the activation energies. In this case it is found from Tables 4 and 6 that caesium reacts faster than potassium, confirming the trend $\mathrm{Na} < \mathrm{K} < \mathrm{Cs}$.

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REFERENCES

[1] C. E. H. Bawn, *Chem. Soc. Ann. Report*, 1974, **36**, 39.

[2] B. G. Gowenlock and K. E. Thomas, *J. Chem. Soc.*, 1965, 5068.

[3] E. U. Emovon and E. A. Lissi, *J. Chem. Soc.*, 1964, 3509.

[4] (*a*) D. S. Boak, N. J. Friswell, and B. G. Gowenlock, *J. Organometallic Chem.*, 1971, **27**, 333; (*b*) D. S. Boak and B. G. Gowenlock, *ibid.*, 1971, **29**, 385.

[5] J. A. Kerr, E. A. Lissi, and A. F. Trotman-Dickenson, *J. Chem. Soc.*, 1964, 1673.

[6] E. U. Emovon and J. F. Ojo, *J. Chem. Soc.* (*B*), 1969, 765.

[7] F. Riding, J. Scanlan, and E. Warhurst, *Trans. Faraday Soc.*, 1956, **52**, 1354.

[8] H. Eyring and R. P. Smith, *J. Amer. Chem. Soc.*, 1952, **74**, 229.

[9] A. I. Vogel, ' Qualitative Inorganic Analysis ', Longman Green, London, 1963, 3rd edn., p. 1044.

[10] ' Dictionary of Organic Compounds ', Eyre and Spottiswoode, London, 1965, vol. 2, p. 650; vol. 3, pp. 1444, 1451; vol. 4, p. 2234.

[11] ' Handbook of Chemistry and Physics ', Chemical Rubber Company, Cleveland, 1969—1970, 50th ed., pp. 285, 287, 441, 159.

[12] A. I. Vogel, ' Textbook of Practical Organic Chemistry ', Longman Green, London, 1963, pp. 733, 516.

[13] J. F. Mckenna, and F. J. Sowa, *J. Amer. Chem. Soc.*, 1937, **59**, 470.

[14] G. A. Olah, S. H. Flood, and M. E. Moffat, *J. Amer. Chem. Soc.*, 1964, **86**, 1065.

[15] M. G. Evans and M. Polanyi, *Trans. Faraday Soc.*, 1938, **34**, 11.

[16] A. Maccoll, *J. Chem. Soc.*, 1955, 965.

[17] R. A. Ogg and M. Polanyi, *Trans. Faraday Soc.*, 1935, **34**, 1375.