far as we have been able to tell, the isomers have never been separated heretofore. In isolating the non-reactive component, samples of purified piperylene were vaporized in a stream of hydrogen and the mixture passed through molten maleic anhydride, the small quantity of hydrocarbon remaining with the effluent gas being condensed and examined.

Piperylene from both sources yielded a condensate which had the same index of refraction, *viz.*, 1.4321, and exhibited only an extremely slow and incomplete reaction with maleic anhydride. The normal corrected boiling point of the substance, as determined in a micro-Cottrell apparatus, was 43.8° as compared to 41.9° of the original purified piperylene. On the basis of the higher boiling point and index, it would appear that the unreactive form is the *cis* isomer, although Provost[3] has reported the boiling points of the *cis* and *trans* forms as 39 and 42.5°, respectively, from distillation data.

Finally, it is believed that the observations mentioned here are of interest not only as a means of isolating what is believed to be *cis*-piperylene, but also from the standpoint of the selectivity of the Diels–Alder condensation in general.

The writers wish to acknowledge the coöperation of Mr. A. L. Ward of the United Gas Improvement Company, who originally called their attention to the discrepancies in the analysis for piperylene in cracked C_5 fractions and to the possibility of the presence of close boiling *cis*- and *trans*-configurations. This work has been done on cracked C_5 fractions furnished by Mr. Ward, and on pure piperylene samples supplied by Messrs. E. R. Gilliland and H. E. Buc.

(3) Provost, *Compt. rend.*, **182**, 1475 (1926).

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The Activity Coefficients of Sodium and Potassium Fluorides at 25° from Isopiestic Vapor Pressure Measurements

BY R. A. ROBINSON[1]

It is known as a result of freezing point determinations[2] that the order of the activity coefficients of the alkali metal fluorides is the reverse of that which holds for the other three halides. The equation developed by Scatchard[3] predicts that the activity coefficients of the alkali metal fluorides should increase with increasing atomic number of the cation, although quantitative agreement with the freezing point results requires a larger radius for the fluoride ion than that obtained from crystallographic data. Scatchard's theory is therefore supported by data at the freezing point. It is of some interest to ascertain whether this reversal in order is also to be found at higher temperatures, and for this purpose isopiestic measurements have been made at 25° on sodium and potassium fluoride. Stock solutions were prepared from Baker C. P. material and the concentrations determined by analysis. The solutions were equilibrated with solutions of potassium chloride with the results given in Table I.

TABLE I

MOLALITIES OF SOLUTIONS OF POTASSIUM CHLORIDE AND SODIUM OR POTASSIUM FLUORIDE WHICH ARE ISOPIESTIC AT 25°

Sodium Fluoride

m_{KCl}	m_{NaF}	m_{KCl}	m_{NaF}
0.1554	0.1562	0.6765	0.6896
.2490	.2504	.7874	.8088
.4047	.4097	.8518	.8734
.5616	.5728	.8908	.9124
.5774	.5870	.9106	.9356

Potassium Fluoride

m_{KCl}	m_{KF}	m_{KCl}	m_{KF}
0.1612	0.1598	2.245	2.086
.3254	.3221	2.484	2.290
.7544	.7353	3.112	2.823
.9904	.9572	3.188	2.873
1.084	1.049	3.761	3.354
1.383	1.316	3.918	3.497
1.568	1.480	3.982	3.526
1.941	1.815	4.580	4.006
2.108	1.964	4.81	4.183

TABLE II

OSMOTIC AND ACTIVITY COEFFICIENTS OF SODIUM AND POTASSIUM FLUORIDE AT 25°

m	φ_{NaF}	γ_{NaF}	m	φ_{NaF}	γ_{NaF}
0.1	0.923	0.764	0.5	0.888	0.631
.2	.909	.708	.7	.880	.602
.3	.899	.675	1.0	.873	.572

m	φ_{KF}	γ_{KF}	m	φ_{KF}	γ_{KF}
0.1	0.929	0.774	1.5	0.958	0.649
.2	.920	.727	2.0	.987	.663
.3	.917	.701	2.5	1.021	.684
.5	.917	.672	3.0	1.054	.713
.7	.922	.657	3.5	1.091	.748
1.0	.934	.649	4.0	1.130	.790

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(1) Sterling Fellow, Yale University, 1940.

(2) Karagunis, Hawkinson and Damköhler, *Z. physik. Chem.*, **151A** 433 (1930).

(3) Scatchard, *Chem. Rev.*, **19**, 309 (1936).

From these data the activity coefficients given in Table II were calculated.

The freezing point data have been used[4] to calculate the activity coefficient of potassium fluoride at 25°. A value of $\gamma = 0.848$ is computed at 0.1 *M*, which is considerably higher than that of other 1–1 electrolytes at this concentration (the value for lithium iodide is 0.811). Referring the freezing point data to $\gamma = 0.774$ at 0.1 *M* and 25°, however, values of 0.736, 0.676, 0.648 and 0.638 at 0.2, 0.5, 1.0 and 2.0 *M*, respectively, are obtained. Except at 2.0 *M*, the agreement with the isopiestic results is moderately good. The freezing point data for sodium fluoride cannot be corrected to 25°; a value of $\gamma = 0.752$ at 0.1 *M* is obtained[4] at 0°, compared with 0.764 at 25°. Referred to the latter value at 0.1 *M*, the freezing point data give $\gamma = 0.703$ and 0.625 at 0.2 and 0.5 *M*, respectively, again in moderate agreement with the isopiestic results.

The activity coefficient of potassium fluoride is very close to that of sodium chloride, while sodium fluoride has a much lower activity coefficient, close to that of rubidium iodide.

[4] Landolt-Börnstein, "Tabellen," Dritter Ergänsungsband, p. 2148.

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The Velocity of Rapid Chlorinations

BY HENRY C. THOMAS

Halford[1] has called attention to the possibility of studying rapid halogenations by measuring the distribution of radioactive halide between product and halide ion when the process is carried out in the presence of tagged halide ions. Long and Olson[2] have shown that the velocity of chlorination of acetanilide is slow compared to the velocity of interchange between chlorine and chloride ion in aqueous solution. Experiments have been carried out to investigate the possibility of measuring the rate of chlorination of an organic molecule with respect to the rate of exchange between chlorine and hydrochloric acid in benzene solution. Benzene was selected as the solvent in the hope that the low degree of dissociation of hydrochloric acid in this medium would bring about a moderately slow exchange reaction.

If it is assumed that the addition of chlorine is slow and that the exchange reaction

$$HCl^* + Cl_2 \rightleftarrows HCl + ClCl^*$$

and the chlorination

$$RH + Cl_2 \longrightarrow RCl + HCl$$

proceed at comparable rates, an expression for the distribution of radioactivity may be obtained as follows. If α is the fraction of Cl_2 exchanging before reacting with the organic molecule; a, the initial number of moles of Cl^- as HCl; θ_0, the initial fraction of Cl^- which is radioactive; and $\theta(x)$, the fraction of Cl^- which is radioactive after the addition of x moles of Cl_2, then

$$(a + x)\theta + \alpha \int_0^x \theta \, dx = a\,\theta_0 \tag{1}$$

where $(a + x)\theta$ and $x\,\theta_p = \alpha \int_0^x \theta \, dx$ are the activities, respectively, of the final solution and of the chlorinated product. Equation (1) may be readily solved, and the ratio of the activity of the product to the initial activity of the solution is found to be

$$x\,\theta_p/a\,\theta_0 = 1 - [a/(a + x)]^\alpha \tag{2}$$

Using the data of Long and Olson[2] one finds $\alpha = 1.04$. This result is unity within the experimental error, indicating, as the authors pointed out, complete exchange between Cl^- and Cl_2 before chlorination. (The experiment of Long and Olson was repeated using different ratios of Cl_2 to Cl^-. Calculated values of α were again unity within experimental error.)

In order to carry out experiments in benzene solution radioactive hydrogen chloride was introduced in the form of the dry gas, prepared directly from sodium chloride which had been bombarded by deuterons. The chlorinations were carried out on *p*-chlorophenol. Chlorine was introduced from a bulb of the gas attached to the flask of solution through a large-bore stopcock. The chlorinated product for radioactive analysis was recovered by distilling the benzene–hydrogen chloride solution through a fractionating column and dilution of the residue to an appropriate volume. The solutions, before and after chlorination, were analyzed for hydrochloric acid content by shaking with water and titration of the mixture. Two chlorinations of *p*-chlorophenol were carried out with the following results

Concn. *p*-ClC_6H_4OH, *m*	a	$a + x$	$x\,\theta_p/a\,\theta_0$
0.403	0.00960	0.01325	0.290
.409	.01045	.01330	.220

[1] R. S. Halford, THIS JOURNAL, **62**, 3233 (1940).

[2] F. A. Long and A. R. Olson, *ibid.*, **58**, 2214 (1936).