[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY]

The Reversible Addition of Sodiodiphenylmethide to Benzophenone in Liquid Ammonia, Base-catalyzed Cleavage of 1,1,2,2-Tetraphenylethanol[1,2]

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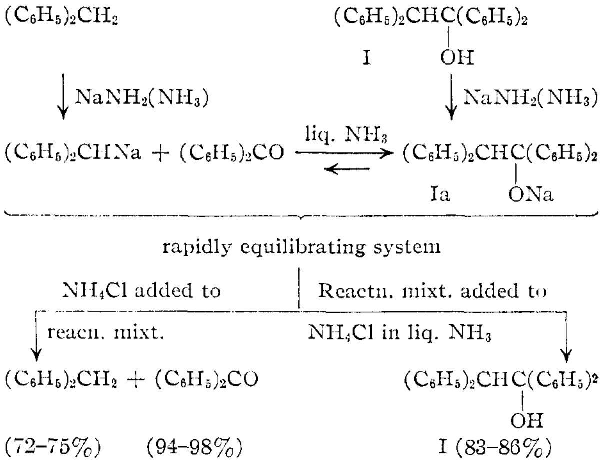
1,1,2,2-Tetraphenylethanol was converted by an equivalent of sodium amide in liquid ammonia to its sodium salt which exhibited the characteristics of the equilibrium system prepared from sodium diphenylmethide and benzophenone. The sodium salt of the carbinol underwent cleavage on adding ammonium chloride, benzyl chloride and sodium amide to form diphenylmethane and benzophenone or derivatives of these products. The derivative with benzyl chloride was the alkylation product of sodium diphenylmethide, and that with sodium amide, the alkali amide–benzophenone adduct. This adduct was shown not to be in equilibrium with sodium diphenylmethide. 1,1,2,2-Tetraphenylethanol was cleaved by catalytic amounts of sodium amide in liquid ammonia and sodium ethoxide in ethanol and tetrahydrofuran to form diphenylmethane and benzophenone. Consideration is given to factors influencing the equilibrium and to mechanisms.

Recently[4] sodium diphenylmethide prepared from diphenylmethane and sodium amide in liquid ammonia was condensed with benzophenone to form the sodium salt of 1,1,2,2-tetraphenylethanol, from which the free carbinol was obtained on instantaneous acidification of the reaction mixture. However, the salt of the carbinol underwent reversion to starting materials when the reaction mixture was acidified gradually.

In the present investigation a study was made of this reversion of the sodium salt of 1,1,2,2-tetraphenylethanol and of certain related reactions including the base catalyzed cleavage of the carbinol.

It was found that the sodium salt of the carbinol prepared from molecular equivalents of the carbinol and sodium amide in liquid ammonia and ether exhibits similar characteristics to those observed previously[4] with the reaction mixture produced from molecular equivalents of sodium diphenylmethide and benzophenone in this medium. Thus, the carbinol was regenerated when the reaction mixture was poured into a solution of excess ammonium chloride in liquid ammonia, whereas diphenylmethane and benzophenone were obtained when solid ammonium chloride was added slowly to the reaction mixture. These results, together with the related earlier ones, are summarized in Scheme A.

SCHEME A

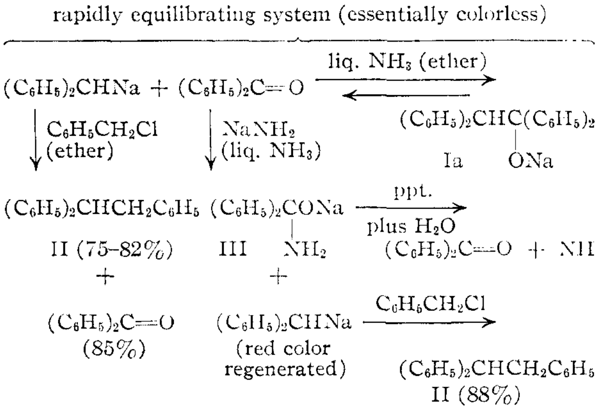


Evidently the same rapidly equilibrating system is set up from the carbinol and sodium amide as from diphenylmethane, sodium amide and benzophenone. The position of the equilibrium of this system is considered to be far on the side of the sodium salt of the carbinol Ia not only from the results given in Scheme A, but also because the system prepared in either manner is essentially colorless. If there were an appreciable concentration of sodium diphenylmethide present, the equilibrium system should have been red since this is the characteristic color of the diphenylmethide ion.[5]

The cleavage of the sodium salt of the carbinol on gradual acidification of the reaction mixture may be accounted for on the basis that the sodium diphenylmethide, which is presumably present in very low concentration, undergoes preferential neutralization.

It seemed possible on this basis that the sodium salt of the carbinol in the equilibrium system might also undergo cleavage on treatment with benzyl chloride and sodium amide, which should be expected to react preferentially with the sodium diphenylmethide and benzophenone, respectively. These expectations were realized (Scheme B).

SCHEME B



It can be seen from Scheme B that the addition of a molecular equivalent of benzyl chloride to the

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(2) A preliminary report was given at the 132nd Meeting of the American Chemical Society at New York, N. Y., Sept. 8–13, 1957.

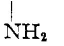
(3) Department of Chemistry, Wake Forest College, Winston-Salem, N. C.

(4) P. J. Hamrick, Jr., and C. R. Hauser, THIS JOURNAL, **81**, 2096 (1959).

(5) It is possible that the sodium diphenylmethide is bound up with benzophenone and ammonia in a colorless complex, perhaps involving a six-atom ring, but the equilibrium system shown in Schemes A and B seems adequate for the present results.

equilibrium system produced hydrocarbon II which is the alkylation product of sodium diphenylmethide. Benzophenone was also isolated. The result was essentially the same when the equilibrium system was prepared either from sodium diphenylmethide and benzophenone or from carbinol I and sodium amide. The 75–82% yield of hydrocarbon II isolated is not as high as that (99%) obtained previously[6] by alkylating the red sodium diphenylmethide reagent itself in liquid ammonia, but the hydrocarbon had to be separated from benzophenone in the present experiments. Even the 75–82% yields of the alkylation product may be considered rather remarkable, since the essentially colorless nature of the equilibrium system indicated that the concentration of the sodium diphenylmethide was very low. Yet this reagent underwent the irreversible alkylation preferentially to the sodium salt of the carbinol Ia, the concentration of which was relatively high.

It can further be seen from Scheme B that the addition of a molecular equivalent of sodium amide to the equilibrium system produced the sodium amide adduct of benzophenone III and sodium diphenylmethide. This cleavage of the sodium salt of the carbinol Ia was particularly striking, since it was accompanied by the appearance of the characteristic red color of the sodium diphenylmethide. Subsequent addition of benzyl chloride to the reaction mixture produced hydrocarbon II in 88% yield. Since the equilibrium system employed in this cleavage experiment was prepared by the addition reaction of sodium diphenylmethide with benzophenone, this red reagent may be said to have been regenerated by another addition reaction involving sodium amide and the ketone to form adduct III. The adduct III was identified not only by its subsequent hydrolysis to benzophenone and ammonia as indicated in Scheme B, but also by treating the original reaction mixture with two equivalents of benzyl chloride. The excess halide alkylated not only the sodium diphenylmethide to give hydrocarbon II (88%) but apparently also the adduct III to form amino-ether IV, which eliminated benzyl alcohol to give benzophenoneimine V. Subsequent hydrolysis of this imine produced benzophenone in an 8% over-all yield.



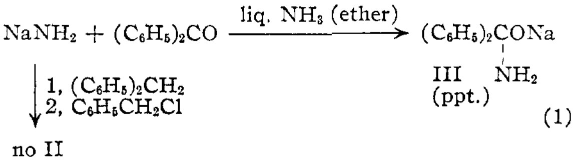
$$\underset{\mathrm{NH_2}}{(C_6H_5)_2\overset{|}{C}OCH_2C_6H_5}$$

IV

$(C_6H_5)_2C{=}NH$

V

The addition reaction of sodium amide to benzophenone is evidently less reversible than that of sodium diphenylmethide to this ketone. In fact, evidence was obtained that the former addition reaction is so complete under the conditions employed that sodium amide is not in mobile equilibrium with adduct III. Thus, on adding benzophenone to an equivalent of sodium amide in liquid ammonia containing some ether, the adduct III precipitated. On adding diphenylmethane followed by benzyl chloride after one hour, no color was produced and none of hydrocarbon II was isolated. Only the starting materials were recovered. Had sodium diphenylmethide been formed in equilibrium, hydrocarbon II should have been obtained. This result may be summarized by equation 1.

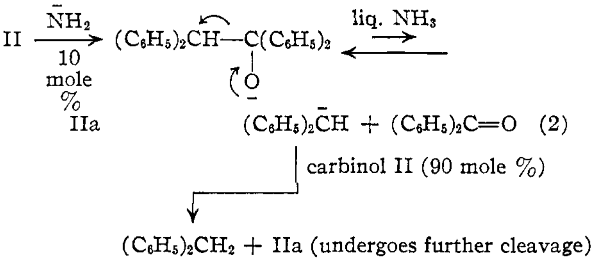


$$\mathrm{NaNH_2} + (C_6H_5)_2CO \xrightarrow{\text{liq. NH}_3\text{ (ether)}} \underset{\substack{\text{III}\quad \mathrm{NH_2}\\ \text{(ppt.)}}}{(C_6H_5)_2CONa} \qquad (1)$$

$$\downarrow \text{1, } (C_6H_5)_2CH_2;\ \text{2, } C_6H_5CH_2Cl \quad \text{no II}$$

That adduct III was precipitated was shown by hydrolysis to form benzophenone and ammonia and by cleavage in refluxing benzene to give benzamide. This cleavage is well known.[7]

Base-catalyzed Cleavage of Carbinol I.—Since the sodium salt of the carbinol underwent cleavage on gradually reducing the basicity of the medium by adding solid ammonium chloride (see Scheme A), the carbinol itself might be expected to undergo cleavage on treatment with a catalytic amount of sodium amide in liquid ammonia. Such a cleavage of the carbinol was realized in the presence of 10 mole per cent. of sodium amide in liquid ammonia and a little ether to form diphenylmethane (87%) and benzophenone (95%). This cleavage must have been brought about by the catalytic amount of the amide ion and not merely during the subsequent neutralization, since the reaction mixture was poured into excess ammonium chloride in liquid ammonia under which conditions the carbinol I has been recovered from its salt (see Scheme A). The mechanism for the cleavage may be represented by equation 2



$$\text{II} \xrightarrow[\substack{10\\ \text{mole}\\ \%}]{\bar{\mathrm{N}}\mathrm{H_2}} \underset{\text{IIa}}{} (C_6H_5)_2CH{-}\underset{\bar{O}}{\overset{}{C}}(C_6H_5)_2 \underset{}{\overset{\text{liq. NH}_3}{\rightleftarrows}} (C_6H_5)_2\bar{C}H + (C_6H_5)_2C{=}O \quad (2)$$

$$(C_6H_5)_2\bar{C}H \xrightarrow{\text{carbinol II (90 mole \%)}} (C_6H_5)_2CH_2 + \text{IIa (undergoes further cleavage)}$$

In this mechanism only a small amount (10 mole per cent.) of the carbinol I is converted at one time to its sodium salt.[8] The anion of this salt gradually β-eliminates the diphenylmethide ion which is neutralized by the carbinol thereby allowing the cleavage to continue. This amounts to the preferential neutralization of the diphenylmethide ion by the carbinol I as indicated in equation 2. This is similar to the preferential neutralization of the diphenylmethide ion that occurs on adding solid ammonium chloride to the equilibrium system (see Scheme A).

Also, carbinol I underwent cleavage in the presence of 10 mole per cent. of sodium ethoxide in ethanol and tetrahydrofuran to form diphenylmethane (72%) and benzophenone (95%). The mechanism would presumably be similar to that shown in equation 2 except that the ethanol as

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[6] C. R. Hauser and P. J. Hamrick, Jr., THIS JOURNAL, **79**, 3142 (1957).

[7] See A. Haller and E. Bauer, *Ann. chim. phys.*, [8] **16**, 146 (1909).

[8] The metallic cation associated with the salt may influence the rate of the cleavage since a somewhat similar cleavage has been shown to be dependent on the metallic cation; C. R. Hauser and W. H. Puterbaugh, THIS JOURNAL, **75**, 4756 (1953).

well as the carbinol may function as the acid that effects the preferential neutralization of the diphenylmethide ion.

Earlier workers[9] have effected the cleavage of carbinol I with excess potassium hydroxide in refluxing ethanol. The fact that this cleavage occurs even with excess hydroxide or ethoxide ion is not surprising since water or ethanol is a sufficiently strong acid to effect the essentially complete neutralization of the diphenylmethide ion present in the equilibrium. On the other hand, liquid ammonia is too weak an acid to effect appreciable neutralization of the diphenylmethide ion so that the sodium salt of the carbinol prepared by means of an equivalent of sodium amide is relatively stable in this medium. Indeed, the condensation of sodium diphenylmethide with benzophenone in liquid ammonia furnishes an excellent method of preparation of the carbinol I and related carbinols.[4]

Factors Influencing the Equilibrium.—The cleavage of carbinol I by a catalytic amount of amide or ethoxide ion in the appropriate medium indicates that diphenylmethane and benzophenone are thermodynamically more stable than the carbinol. Apparently the decrease in free energy that accompanies this cleavage arises from an increase in bond energies[10] and perhaps also from the resonance energy associated with the aromatic ketone.

Since the neutral molecules of diphenylmethane and benzophenone are evidently more stable than the neutral carbinol, the free energy decrease associated with the addition reaction of sodium diphenylmethide with benzophenone in liquid ammonia is suggested to be the formation of the more weakly basic anion of the resulting sodium salt of the carbinol. Although precipitation may increase the yield, the formation of the sodium salt of the carbinol appears to be almost complete even in solution.[4]

Experimental[11]

Conversion of Carbinol I to Salt Ia and Neutralization. (A) Recovery of Carbinol I.—To a stirred suspension of 0.04 mole of sodium amide in 200 ml. of anhydrous liquid ammonia[12] was added 14 g. (0.04 mole) of 1,1,2,2-tetraphenylethanol (I) and 100 ml. of dry ether. After stirring for 30 minutes, the carbinol had dissolved. The resulting essentially colorless solution of the sodium salt of the carbinol Ia was poured into a solution of 8 g. of ammonium chloride in 250 ml. of liquid ammonia. The ammonia was removed on the steam-bath, and the residue was shaken with water. The solid was collected on a funnel, washed with water, and dried. Recrystallization from methylene chloride gave 11.6 g. (83%) of recovered carbinol I.

(B) Cleavage to Form Diphenylmethane and Benzophenone.—The sodium salt of the carbinol Ia was prepared in liquid ammonia and ether as described above in (A). To the stirred solution of this salt was added slowly 8 g. of solid ammonium chloride. The ammonia was removed on the steam-bath as 100 ml. of additional ether was added. The ethereal layer was separated, dried, and evaporated. The residue was treated with 2,4-dinitrophenylhydrazine reagent to give a 94% yield of the 2,4-dinitrophenylhydrazone of benzophenone, m.p. 238–239°, and a 72% yield of diphenylmethane.

Addition of Benzyl Chloride to Equilibrium System. (A) To System Prepared from Sodium Diphenylmethide and Benzophenone.—To a stirred suspension of 0.06 mole of sodium amide in 250 ml. of anhydrous liquid ammonia was added a solution of 10.1 g. (0.06 mole) of diphenylmethane in 50 ml. of dry ether, followed after 5 minutes by a solution of 11 g. (0.06 mole) of benzophenone in 100 ml. of dry ether. To the resulting, stirred mixture (essentially colorless) there was added after 10 min. a solution of 7.6 g. (0.06 mole) of benzyl chloride in 25 ml. of ether. After 30 minutes, the liquid ammonia was removed (steam-bath). The residue was shaken with 100 ml. of ether and 50 ml. of water, and the two layers were separated. The ethereal layer was dried over magnesium sulfate, and the solvent removed. The oily residue was distilled *in vacuo* to give foreruns of benzyl chloride and diphenylmethane, and 9.8 g. (85%) of benzophenone, b.p. 171–177° at 10 mm., m.p. 47–48°; m.p. 2,4-dinitrophenylhydrazone 239°. The residue remaining in the flask was crystallized from ethanol to give 12.5 g. (82%) of 1,1,2-triphenylethane (II), m.p. 53–54°; reported m.p. 54°[13] and 56°.[14] A mixed melting point with an authentic sample of this hydrocarbon[6] showed no depression.

(B) To System Prepared from Carbinol I and Sodium Amide.—To a stirred suspension of 0.02 mole of sodium amide in 250 ml. of liquid ammonia was added 7 g. (0.02 mole) of 1,1,2,2-tetraphenylethanol (I) and 100 ml. of ether. After 10 minutes, 2.53 g. (0.02 mole) of benzyl chloride was added. The ammonia was replaced by ether, and the resulting suspension was shaken with aqueous ammonium chloride. The ethereal layer was separated, dried, and the solvent removed. The residue was taken up in ethanol, and a few drops of water were added. Scratching induced crystallization to give 3.9 g. (75%) of 1,1,2-triphenylethane (II), m.p. 55–56° after recrystallization from ethanol. Benzophenone was isolated as its 2,4-dinitrophenylhydrazone from the alcoholic solutions.

Treatment of Equilibrium Mixture with Sodium Amide.—To a stirred, red solution of sodium diphenylmethide prepared from 0.06 mole of sodium amide in 250 ml. of anhydrous liquid ammonia and 0.06 mole of diphenylmethane in 50 ml. of dry ether there was added 0.06 mole of benzophenone in 50 ml. of dry ether. To the resulting essentially colorless solution there was added 0.06 mole of sodium amide in 100 ml. of liquid ammonia. The red color reappeared immediately. After 15 minutes, 15.18 g. (0.12 mole) of benzyl chloride in 50 ml. of ether was added. The red color was again discharged (after 0.06 mole of the halide was added). After 4 hours (Dry Ice–acetone condenser), the liquid ammonia was removed (steam-bath). Additional ether (100 ml.) was added and the resulting ethereal suspension was filtered. The solid on the funnel (adduct III) was treated with water (ammonia evolved), and the resulting mixture was worked up to give 7.3 g. (33%) of benzophenone 2,4-dinitrophenylhydrazone, m.p. and mixed m.p. 238–239°. The ethereal filtrate was concentrated to about 100 ml. and saturated with dry hydrogen chloride to precipitate benzophenone imine hydrochloride. The mixture was filtered, and the solid was treated with water to produce an oil, from which there was isolated 2.8 g. (8%) of benzophenone 2,4-dinitrophenylhydrazone, m.p. 239°. The ethereal filtrate (containing hydrogen chloride) was evaporated. The residual yellow oil was distilled *in vacuo* to give 9.9 g. of recovered benzyl chloride, b.p. 62° at 10 mm.; 9.2 g. (52%) of benzophenone, b.p. 166–167° at 8 mm., and 22.8 g. (88%) of 1,1,2-triphenylethane (II) b.p. 153–154° at 1 mm., m.p. 54–55° (after recrystallization from 95% ethanol). Hydrocarbon II was identified by the mixed melting point method.

Treatment of Adduct III with Diphenylmethane and Benzyl Chloride.—To a stirred suspension of 0.06 mole of sodium amide in 250 ml. of liquid ammonia there was added a solution of 11 g. (0.06 mole) of benzophenone in 50 ml. of dry ether. A gray precipitate of adduct III formed. After 5 minutes, 10 g. (0.06 mole) of diphenylmethane in 50 ml. of dry ether was added. No red color was observed. After one hour, 7.6 g. (0.06 mole) of benzyl chloride in 25 ml. of ether was added. The mixture was stirred for 2 hours, and the liquid ammonia was evaporated. The resulting

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[9] C. F. Koelsch, THIS JOURNAL, **53**, 1147 (1931); D. Y. Curtin and S. Leskowitz, *ibid.*, **73**, 2630 (1951).

[10] Professor George Glockler of this department has estimated that the cleavage is accompanied by a decrease in heat content of approximately 7 kcal./mole based on a set of bond energies appropriate for the types of molecules involved.

[11] Melting points and boiling points are uncorrected.

[12] See C. R. Hauser, F. W. Swamer and J. T. Adams, "Organic Reactions," Vol. VIII, John Wiley and Sons, Inc., New York, N. Y., 1954, p. 122.

[13] A. Klages and S. Heilmann, *Ber.*, **37**, 1455 (1904).

[14] W. Schlenk and E. Bergmann, *Ann.*, **463**, 44 (1928).

ethereal suspension was stirred for one hour, and then filtered. The solid was treated with water to evolve ammonia and produce an oil from which there was isolated 8 g. (77%) of benzophenone, b.p. 166–167° at 8 mm., identified as its 2,4-dinitrophenylhydrazone. The ethereal filtrate was evaporated, and the residue was distilled to give 6.03 g. (80%) of benzyl chloride, b.p. 67–69° at 20 mm., and 9.5 g. (94%) of diphenylmethane, b.p. 121–123° at 10 mm.

The gray precipitate of adduct III was prepared again and the diphenylmethane then added as described above. The ammonia was removed and the resulting ethereal suspension was filtered. A portion of the solid was hydrolyzed to give ammonia and benzophenone, isolated as its oxime, m.p. 143–144°. Another portion of the solid was heated in toluene for 3 hours to give benzamide, m.p. and mixed m.p. 127–128°, and a relatively small amount of benzoic acid, m.p. 121°.

Base-catalyzed Cleavage of Carbinol I. (A) With Sodium Amide.—Eight grams of 1,1,2,2-tetraphenylethanol (I) was added to 10 mole per cent. of sodium amide in 200 ml. of liquid ammonia and 50 ml. of ether. The liquid ammonia was allowed to reflux under a Dry Ice–acetone condenser until all of the solid had dissolved (about 2 hr.). The reaction mixture was poured into excess of ammonium chloride in liquid ammonia. The ammonia was removed, and ether and water were added. The ethereal layer was combined with an ether extract of the aqueous layer. The ethereal solution was dried over Drierite, and the solvent removed. The oily residue was treated with 2,4-dinitrophenylhydrazine reagent, and the resulting precipitate of the 2,4-dinitrophenylhydrazone of benzophenone was removed. The yield was 95%. From the filtrate there was isolated an 87% yield of diphenylmethane, b.p. 116–123° at 10 mm. No unreacted carbinol I was recovered.

(B) With Sodium Ethoxide.—To 100 ml. of absolute ethanol containing 50 ml. of tetrahydrofuran was added 0.12 g. of sodium metal. When the metal had dissolved, 17.5 g. (0.05 mole) of carbinol I was added and the mixture was refluxed in a system protected from atmospheric moisture by a drying tube. All the solid did not dissolve even in the boiling solution. Overnight heating gave a homogeneous solution. Glacial acetic acid (1 ml.) was added to the solution and the solvent was evaporated on the steam-bath under aspirator vacuum to a volume of about 25 ml. The solution was treated with 2,4-dinitrophenylhydrazine reagent and the resulting precipitate of the 2,4-dinitrophenylhydrazone of benzophenone, m.p. 238–239°, was removed. The yield was 95%. From the filtrate there was isolated a 72% yield of diphenylmethane, b.p. 119–121° at 10 mm. No unreacted carbinol was recovered.

DURHAM, N. C.

COMMUNICATIONS TO THE EDITOR

DIFFUSION COEFFICIENTS OF H_2O–D_2O MIXTURES

Sir:

Adamson and Irani[1] measured the diffusion coefficients of liquid H_2O–D_2O mixtures and found a pronounced minimum at roughly equimolal composition. This curious behavior, which was *not* observed for H_2O^{18} trace diffusion, implies strange limitations on the mechanism of proton migration in water, and it seemed important to reinvestigate the problem by a different technique. Using the porous-frit method,[2,3,4] we have obtained the results given in Table I. The diffusion coefficients are in good agreement with earlier observations (see reference 1) made at low deuterium concentrations, but show little composition dependence.

TABLE I

DIFFUSION COEFFICIENTS OF H_2O–D_2O MIXTURES AT 25.0 ± 0.4°

c_i[a]	c_o[b]	$D \times 10^5$, cm.^{2} sec.$^{-1}$
24	0	2.29
60	24	2.32
55	35	2.20
100	0	2.26

[a] Initial weight % D_2O inside frit. [b] Initial weight % D_2O outside frit.

An unglazed Selas frit was used in all runs and was calibrated with aqueous potassium chloride. To determine whether we could detect significant variations of D with composition, several experiments were made with concentrated calcium chloride solutions. These results and the calibrations with potassium chloride are summarized in Table II, where the subscripts i and o refer to the solutions inside and outside the frit, respectively. The values of D_i and D_o are those of Lyons and Riley[5] for calcium chloride and of Gosting[6] for potassium chloride. The last column gives the diffusion constants found in our experiments.

TABLE II

DIFFUSION COEFFICIENTS OF AQUEOUS SALT SOLUTIONS AT 25°

Salt	c_i[a]	c_o[a]	$D_i \times 10^5$	$D_o \times 10^5$	$D_{obs} \times 10^5$
KCl	2.0	1.0	2.00	1.89	(1.91)[b]
	2.5	0	2.06	1.93	1.94
$CaCl_2$	6	2	0.40	1.31	1.34
	4	2	1.08	1.31	1.35
	6	4	0.40	1.08	0.87
	2	4	1.31	1.08	1.29
	2	6	1.31	0.40	0.78
	4	6	1.08	0.40	0.74

[a] Salt concentrations in moles liter^{-1}. [b] Value assumed for calibration.

For the first two calcium chloride runs, the observed D is close to that for the outside solution, as suggested by Wall and Wendt[7] and by Wagner[8]; but for the others it is closer to the mean of D_i and D_o. Convection is a possible source of error.[9] However, the density differences between inside and outside solution in the calcium chloride runs were greater than for the experiments of Table I.

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[1] A. W. Adamson and R. R. Irani, THIS JOURNAL, **79**, 2967 (1957).

[2] F. T. Wall, P. F. Grieger and C. W. Childers, *ibid.*, **74**, 3562 (1952).

[3] G. B. Taylor and F. T. Wall, *ibid.*, **75**, 6340 (1953).

[4] F. Grün and C. Blatter, *ibid.*, **80**, 3838 (1958).

[5] P. A. Lyons and J. F. Riley, *ibid.*, **76**, 5216 (1954).

[6] L. J. Gosting, *ibid.*, **72**, 4418 (1950).

[7] F. T. Wall and R. G. Wendt, *J. Phys. Chem.*, **62**, 1581 (1958).

[8] C. Wagner, *Trans. AIME*, **44**, 91 (1952).

[9] R. H. Stokes, THIS JOURNAL, **72**, 763 (1950).