TABLE OF ANALYSES

DRIED IN A VACUUM AT ROOM TEMPERATURES

	Calcd. for $Ce_2I_3N_{13}H_{36}$	1	2	3	4
Ce	31.87	32.5	31.9	30.8	32.7
N	20.70	20.5	20.3	21.3	19.4
I	43.30	42.9	43.0	43.0	43.1

HEATED IN A VACUUM AT 150–180°

	Calcd. for $Ce_2I_3N_2H_3$				
Ce	40.50	41.1	39.9	39.5	41.0
N	4.05	4.2	4.7	4.0	3.4
I	55.02	54.2	53.8	55.2	54.0

this precipitate to form cerous thiocyanate and selenocyanate,[5] respectively, neither of which could be crystallized, and so obtained in a pure condition, because of their high solubilities. When a solution of potassium amide in liquid ammonia is poured into one of cerous thiocyanate there results a flocculent yellow precipitate, which at first dissolves, becoming permanent only after further additions of amide. This indicates the formation of a soluble ammonobasic thiocyanate. The precipitate was not a pure cerous amide, imide or nitride. (Cerium content too low. Calcd. for $Ce(NH_2)_3$: Ce, 74.4. Found, 64–72.)

Summary

The ammonobasic iodide, $CeI_3 \cdot Ce(NH_2)_3 \cdot 10NH_3$ and its deammonation product, $CeI_3 \cdot Ce(NH)NH_2$, have been prepared.

STANFORD UNIVERSITY, CALIF. RECEIVED MAY 24, 1937

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(5) *Cf.* Bergstrom, THIS JOURNAL, **48**, 2319 (1926).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, WASHINGTON SQUARE COLLEGE, NEW YORK UNIVERSITY]

The Rate of Dissolution of Benzoic Acid in Dilute Aqueous Alkali

BY CECIL V. KING AND S. S. BRODIE

If a crystal of barium hydroxide is dipped into a rapidly stirred solution of dilute acid containing phenolphthalein, a thin layer of solution at the surface of the crystal becomes pink. The thickness of the alkaline layer varies with the stirring speed, and, if the latter is very low, irregular streamers of alkaline solution may extend one or two centimeters out into the solution. With a very soluble base, as sodium hydroxide, even a high stirring speed cannot confine the alkaline solution to a thin, even layer.

The Nernst diffusion layer theory of dissolution rates predicts this behavior; it assumes that the base saturates a monomolecular film of liquid next its surface so rapidly that a layer is formed in which concentration gradients of both acid and base exist, due to their neutralization within the layer. This type of system was discussed briefly by Brunner[1] but no systematic study of such cases has been made.

If solid benzoic acid is immersed in an alkaline solution a similar gradient of acid and base concentrations should exist near the surface. It will be shown in this paper that the equations based on this assumption account satisfactorily for the dissolution rate of solid benzoic acid in dilute sodium and potassium hydroxide solutions. Benzoic acid was chosen for study because test cylinders with smooth, even surfaces can be prepared, the solubility in water is low and accurately known and the dissolution rate in water has been measured by several investigators.[2–4]

We shall assume, as an approximation, that the Nernst–Brunner treatment is essentially correct for this system. Let δ be the total thickness of the diffusion layer, $\delta - y$ the distance from the surface at which neutralization occurs. Then the rate of dissolution and neutralization will be given by Fick's law as

$$\frac{dx}{dt} = \frac{AD_A s}{\delta - y} = \frac{AD_B c}{y} \qquad (1)$$

where x is the amount dissolved in time t, A is the surface area of the solid, D_A and D_B are the diffusion coefficients of acid and base, respectively, s is the solubility of the acid and c the concentration of the base, all in suitable units.

Actually, it is known that the effective thickness of the diffusion layer varies with the diffusion coefficient of the reagent.[5,6] The variation is not great over the range considered here and little error is introduced by neglecting this factor.

Many investigators believe that the outer surface of the diffusion layer is diffuse and ragged and that the average concentration gradient is not linear over a considerable fraction of the total layer thickness. The experiment described above with barium and sodium hydroxides indicates that

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(1) Brunner, *Z. physik. Chem.*, **47**, 56 (1904).

(2) Noyes and Whitney, *ibid.*, **23**, 689 (1897).

(3) Bruner and St. Tolloczko, *ibid.*, **35**, 283 (1900).

(4) Wildermann, *ibid.*, **66**, 445 (1909).

(5) King, THIS JOURNAL, **57**, 828 (1935).

(6) King and Howard, *Ind. Eng. Chem.*, **29**, 75 (1937).

the lower the concentration differences and the better the stirring, the sharper the boundary of the diffusion layer. In the experiments described in this paper two possibilities may be considered: (1) the zone in which solutes are transported both by convection and diffusion may be negligibly thin compared to the entire layer in which concentration gradients exist; or (2) y and $\delta - y$ may be considered as "effective thicknesses" without destroying the validity of the relation to be derived.

From equation (1)

$$y = D_{\mathrm{B}}c\,\delta/(D_{\mathrm{A}}s + D_{\mathrm{B}}c) \qquad (2)$$

and substituting (2) in (1)

$$\frac{\mathrm{d}x}{\mathrm{d}t} = \frac{A}{\delta}\,(D_{\mathrm{A}}s + D_{\mathrm{B}}c)$$

Replacing s and c by a/V and $(b - x)/V$, where a is the amount of benzoic acid soluble in the volume V, $b - x$ the amount of base left in the same volume at time t

$$\frac{\mathrm{d}x}{\mathrm{d}t} = \frac{AD_{\mathrm{A}}}{\delta V}\,a + \frac{AD_{\mathrm{B}}}{\delta V}\,(b - x) = \frac{A}{V}\,[k_{\mathrm{A}}a + k_{\mathrm{B}}\,(b - x)]$$

Integrating and setting $x = b$ at the time t_1 (when all base is just neutralized)

$$k_{\mathrm{B}} = \frac{2.3V}{At_1}\log\left(1 + \frac{D_{\mathrm{B}}}{D_{\mathrm{A}}} \times \frac{b}{a}\right) = \frac{2.3V}{At_1}\log\left(1 + \frac{k_{\mathrm{B}}}{k_{\mathrm{A}}} \times \frac{b}{a}\right) \qquad (3)$$

Using V in cc., A in sq. cm., t in seconds, K_{B} is obtained in cm./sec. Since D_{B}, D_{A}, b and a enter as ratios, their units are unimportant; the diffusion coefficients were determined independently and are recorded in sq. cm./day, and b and a are expressed in moles.

Since the diffusion coefficients are considerably influenced by salts and the benzoate concentration at the acid surface is unknown, equation (3) was solved by approximating the ratio $D_{\mathrm{B}}/D_{\mathrm{A}}$ or $k_{\mathrm{B}}/k_{\mathrm{A}}$, the best value being that which makes k_{B} constant over a range of base concentrations. The ratios found in this manner can be checked against the experimental ratios of the diffusion coefficients. The constants k_{A} and k_{B} are, respectively, rate constants for benzoic acid dissolving in water (or salt solution) and for an acid which itself is completely insoluble but whose salts are soluble in water, dissolving in sodium and potassium hydroxides. Values of k_{A} were determined independently and are compared with values calculated from equation (3).

Experimental

Some difficulty was encountered in preparing benzoic acid cylinders suitable for accurate rate measurements. The method finally adopted was as follows: hard rubber cylinders (to which the molten acid adheres well) 7.62 cm. long and 2.0 cm. in diameter were fitted with short steel end-pieces 2.2 cm. in diameter. A layer of benzoic acid 1 mm. thick was built up by repeatedly dipping the cylinder in the molten acid, scraping the steel ends between dippings. This left cylinders of uniform diameter and smooth ends, with no cracks in the hard, glassy surface layers. The steel end pieces were replaced with hard rubber nuts before use. No more than 0.005 mole could be dissolved from such a cylinder safely; contrary to statements in the literature, a rough or pitted surface increased the dissolution rate considerably. When larger amounts of base were present, two or more such cylinders were used.

The best grade of resublimed benzoic acid was used for the final experiments. Another brand with almost identical analysis but apparently purified by recrystallization was found useless for the purpose; it darkened quickly on melting, did not adhere well to the rubber, and left brittle, crumbly cylinders. U. S. P. acid formed good cylinders, but dissolved several per cent. faster, perhaps because of a greater solubility in pure water. All experiments were run at 25 ± 0.5°.

Rate Measurements in Sodium Hydroxide.—In these experiments benzoic acid cylinders were rotated in 500 cc. of solution until the color of phenolphthalein faded. If more than 0.005 mole of base was present, two or more cylinders were used. The time t_1 could be duplicated to ± three seconds. Multiples of 25 cc. of carbonate-free stock solution of sodium hydroxide, 0.1545

TABLE I

Rate Constants in Sodium Hydroxide. Cylinders 2.2 cm. diameter, 7.62 cm. length; 500 cc. solution, 25°.

Cc. NaOH (0.1545 M)		25	50	75	100	125	150
				2000 r. p. m.			
t_1, sec.		240	390	511	602	677	728
$\frac{D_{\mathrm{B}}}{D_{\mathrm{A}}} =$	2.2	0.0189	0.0195	0.0194	0.0195	0.0196	0.0201
	2.6	.0215	.0218	.0214	.0214	.0214	.0218
	3.0	.0241	.0239	.0233	.0232	.0231	.0233
				3000 r. p. m.			
t_1, sec.		163	271	341	390	453	489
$\frac{D_{\mathrm{B}}}{D_{\mathrm{A}}} =$	2.2	0.0278	0.0281	0.0290	0.0302	0.0294	0.0300
	2.6	.0318	.0314	.0322	.0331	.0321	.0326
	3.0	.0354	.0344	.0349	.0358	.0344	.0348
				4000 r. p. m.			
t_1, sec.		122	190	255	301	...	369
$\frac{D_{\mathrm{B}}}{D_{\mathrm{A}}} =$	2.2	0.0372	0.0400	0.0389	0.0390	...	0.0397
	2.6	.0424	.0448	.0430	.0429	...	.0431
	3.0	.0474	.0492	.0467	.0463	...	.0461

M, were diluted to 500 cc. for each experiment. Details are given in Table I with calculated values of k_B for three values of the ratio D_B/D_A. The solubility of benzoic acid was taken as 0.0276 mole per liter at 25°.

At the stirring speed 2000 r. p. m. the values of k_B show the best constancy with the ratio $D_B/D_A = 2.6$. At the higher stirring speeds the best value of the ratio is somewhat higher, about 2.7.

Rate Measurements in Potassium Hydroxide.—The preceding experiments were repeated with potasium hydroxide, which has a somewhat higher diffusion coefficient than sodium hydroxide. A stock solution 0.1903 *M* was used, and multiples of 20.3 cc. (equivalent to 25 cc. of the sodium hydroxide solution) were diluted to 500 cc. The dissolution rates are decidedly different from those in sodium hydroxide. Details of the experiments are given in Table II. The best values of K_B are obtained with the ratio of D_B/D_A = 2.8 to 3.0.

TABLE II

Rate Constants in Potassium Hydroxide. Cylinders 2.2 cm. diameter, 7.62 cm. length; 500 cc. solution, 25°.

Cc. KOH (0.1903 *M*)		20.3	40.6	60.9	81.2	121.8
		2000 r. p. m.				
t_1, sec.		234	380	485	564	698
$\frac{D_B}{D_A}$ =	2.6	0.0221	0.0224	0.0226	0.0229	0.0228
	3.0	.0247	.0246	.0246	.0248	.0244
	3.4	.0270	.0266	.0264	.0264	.0258
		3000 r. p. m.				
t_1, sec.		155	254	321	381	462
$\frac{D_B}{D_A}$ =	2.6	0.0334	0.0335	0.0342	0.0339	0.0344
	3.0	.0373	.0367	.0371	.0366	.0368
	3.4	.0408	.0397	.0397	.0390	.0390
		4000 r. p. m.				
t_1, sec.		117	192	240	285	342
$\frac{D_B}{D_A}$ =	2.6	0.0444	0.0444	0.0456	0.0454	0.0465
	3.0	.0494	.0486	.0497	.0489	.0498
	3.4	.0541	.0526	.0532	.0522	.0528

Change of Area and Volume.—A few experiments were carried out with a cylinder 6.38 cm. long and others with the usual cylinders (7.62 cm. long) but with 1000 and 2000 cc. of solution instead of 500 cc. Table III shows the values of t_1 obtained compared with values calculated from equation (3). For the first two experiments the time t_1 is inversely proportional to the cylinder length. For the last three, the ratio D_B/D_A = 2.6 and the value $k_B = 0.0215$ were inserted in equation (3), with appropriate values of *b* and *a*.

TABLE III

Effect of Changed Area of Cylinders and Volume of Solution. Diameter of Cylinders 2.2 cm.; 2000 r. p. m. 25°.

Cc. NaOH (0.1545 *M*)	Cylinder length, cm.	V, cc.	t_1, sec.	t_1, calcd.
25	6.38	500	288	285
50	6.38	500	469	466
50	7.62	1000	481	481
100	7.62	1000	786	790
50	7.62	2000	542	541

Change of Viscosity with Sucrose.—Diffusion coefficients are in general almost, if not quite, inversely proportional to the viscosity in solutions of sucrose, glycerol, etc. In equation (3), increase of viscosity leaves the ratio D_B/D_A practically unchanged, but since D_B is incorporated in k_B, the latter will be inversely proportional to the viscosity, or t_1, as compared to the values of Table I, will increase in direct proportion to the viscosity. In Table IV are given the results of experiments with sucrose up to 1.2 molar added to the alkaline solution, with values of t_1 corresponding to the viscosity ratios η/η_0. The latter were calculated from values in the "International Critical Tables." The viscosity of the sodium hydroxide solutions was considered to be the same as that of water. It was also assumed that the sucrose has no effect on the solubility of benzoic acid. A change of 5% in the solubility would change the calculated values of t_1 by about 3%.

TABLE IV

EFFECT OF SUCROSE ON THE DISSOLUTION RATE. 25 CC. OF 0.1545 *M* NaOH IN 500 CC. OF SOLUTION, 2000 R. P. M., 25°, CYLINDERS 7.62 CM. LENGTH AND 2.2 CM. DIAMETER

C_{sucrose}, *M*	η/η_0	t_1, sec.	t_1, calcd.
0	1	240	(Table I)
0.3	1.41	335	338
.6	1.80	437	432
.9	2.63	632	631
1.2	3.70	889	889

Effect of Added Sodium Acetate.—Benzoic acid becomes more soluble in the salt of a weaker acid because of the reaction which occurs. The solubility in solutions of salts of various weak acids has been measured by Philip.[7] Sodium acetate was chosen to add to the alkaline solutions because the solubility of benzoic acid has suitable values in its solution, and because the diffusion coefficient of acetic acid is only slightly less than

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(7) Philip, *J. Chem. Soc.*, **87**, 987 (1905).

that of benzoic acid in water. It is little affected by acetates,[8] and is probably almost the same as that of benzoic acid in the mixed acetate–benzoate solution near the surface of the solid benzoic acid.

Philip's values were plotted and solubilities interpolated from the smooth curve are given in Table V. These were used in calculating values of t_1 as shown. His value for the solubility in water (0.0289 m. p. l.) is between 3 and 5% higher than other investigators give.[9] An error of 5% in any of the other values would change the calculated t_1 by about 3%.

TABLE V

Effect of Sodium Acetate on the Dissolution Rate. 500 cc. solution, 25°, 2000 r. p. m., cylinders 7.62 cm. long, 2.2 cm. diameter.

		25 cc. NaOH (0.1545 M)		50 cc. NaOH (0.1545 M)		20.3 cc. KOH (0.1903 M)	
$C_{NaC_2H_3O_2}$, M	Solubility benzoic acid, m. p. l.	t_1, sec.	t_1, calcd. ^{a}	t_1, sec.	t_1, calcd. ^{a}	t_1, sec.	t_1, calcd. ^{b}
0	(0.0276)	(240)	...	(390)	...	(234)	...
0.01	.037	187	191	322	323	183	185
.02	.045	163	162	272	280	154	158
.03	.052	147	144	251	253	137	140
.04	.0585	127	130	224	231	121	127
.06	.0705	111	111	200	199	104	108

[a] Equation (3): $0.0215 = (2.3V/At_1) \log (1 + 2.6\ b/a)$.
[b] Equation (3): $0.0236 = (2.3V/At_1) \log (1 + 2.8\ b/a)$.

Rate Constants in Water.—A few measurements of the dissolution rate in pure water were made for the purpose of calculating k_A. One, two or three cylinders 7.62 cm. long, 2.2 cm. in diameter were rotated two, three or six minutes in 500 cc. of carbon dioxide-free water and the solutions titrated with sodium hydroxide after aspirating with carbon dioxide-free air. Otherwise, good unimolecular constants were not obtained. Values of k_A were calculated from the equation

$$k_A = \frac{2.3V}{At} \log \frac{a}{a - x}$$

and a few of them are given in Table VI compared with values calculated from the equality $D_B/D_A = k_B/k_A$ as shown.

These rates show no evidence of reaching a maximum as the stirring speed is increased up to 3000 r. p. m. Wildermann[4] thought that a maximum rate was reached at a rather low stirring speed; he was misled by a moderate experimental error and insufficient variation in stirring speed.

TABLE VI

RATE CONSTANTS IN WATER AT 25°

R. p. m.	k_A, exptl.	k_A, calcd.
1000	0.00437	....
2000	.00899	0.0083^a
2000	.00870	.0084^b
3000	.0130	.0124^a
3000	.0131	.0127^b

[a] From values for sodium hydroxide, $2.6 = 0.0215/k_A$ and $2.6 = 0.0322/k_A$. [b] From values for potassium hydroxide, $2.8 = 0.0235/k_A$ and $2.8 = 0.0355/k_A$.

Diffusion Coefficients.—The diffusion coefficients of benzoic acid and sodium hydroxide were measured in water and in sodium benzoate solutions, and that of potassium hydroxide in water and in potassium benzoate solutions.[10] Porous glass disk cells of the type described by McBain and Dawson[11] were used. The cells were placed in a thermostat at 25 ± 0.02° for twenty-four to forty-eight hours for each run. The values obtained are given in Table VII and shown graphically in Fig. 1. The diffusion coefficient of the acid decreases linearly with the benzoate concentration; the coefficients of the bases increase greatly and apparently reach maxima in the presence of sufficient salt.[12]

TABLE VII

DIFFUSION COEFFICIENTS OF BENZOIC ACID, SODIUM AND POTASSIUM HYDROXIDES IN BENZOATE SOLUTIONS, 25°

Benzoic acid 0.01 M		Sodium hydroxide 0.0213 M		Potassium hydroxide 0.020 M	
$C_{sodium\ benzoate}$, M	D, sq. cm./day	$C_{sodium\ benzoate}$, M	D, sq. cm./day	$C_{potassium\ benzoate}$, M	D, sq. cm./day
0	0.96	0	1.65	0	2.45^a
0.044	.89	0.022	2.62	0.021	3.00
.055	.88	.044	2.97	.052	3.26
.110	.77	.088	3.31	.105	3.52
.220	.60	.110	3.38	.209	3.52
		.184	3.45		

[a] This value is high, probably because the solution was not carbonate-free.

Discussion

An equation of the type $dx/dt = k_1s + k_2c$ can, of course, be derived on the basis of other postulates. One important test of the assumptions made in deriving equation (3) lies in a comparison of the ratio k_B/k_A or D_B/D_A with the ratio of diffusion coefficients obtained independently. The values 2.6–3.0 which satisfy equation (3) best, correspond to the experimental diffusion coefficient ratio at a benzoate concentration of approximately 0.01 M. Unfortunately, the benzoate

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[8] King and Cathcart, THIS JOURNAL, **59**, 63 (1937).

[9] (a) K. W. Haeseler, Ph.D. Dissertation, Columbia University, 1929; (b) H. N. K. Rördam, Ph.D. Dissertation, University of Copenhagen, 1925; (c) Hoffman and Langbeck, *Z. physik. Chem.*, **51**, 385 (1905).

[10] Measurements made by Wm. H. Cathcart.

[11] McBain and Dawson, THIS JOURNAL, **56**, 52 (1934).

[12] King and Cathcart, *ibid.*, **58**, 1639 (1936).

concentrations actually present at the benzoic acid surface cannot be estimated and presumably change with the hydroxide concentration; probably the ratio D_B/D_A actually changes during each experiment and constancy of k_B with changing hydroxide concentration should not be expected. Logically, all the experiments should have been carried out in solutions containing 0.1 to 0.2 M benzoate, in which the hydroxide diffusion coefficients approach their maxima; this was not known at the time the dissolution rate experiments were made. A few experiments in which various amounts of benzoate up to about 0.03 M were added showed no appreciable change in the time t_1 (within three seconds).

A second point of interest is the comparison of rates in sodium and potassium hydroxide solutions. There is no doubt that the difference in rates corresponds well to the difference in diffusion coefficients, and cannot be explained by the slight difference in viscosities or other properties of the solutions.

The dissolution rates in sodium acetate solutions are completely and satisfactorily explained by equation (3) with values of the constants obtained from experiments in solutions of the bases alone. Also, the calculation of the dissolution rates in water alone (Table VI) is reasonably satisfactory.

Perhaps the best evidence for the validity of the assumptions made is the correlation of the rate constants with constants for other diffusion-controlled reactions. In a previous paper[5] it was shown that there is a close relation between rate constants for a number of such reactions and diffusion coefficients (probably an exponential relation).[6] Values of rate constants used there were, in cm./min.: for benzoic acid alone 0.71, for sodium hydroxide (k_B) 1.75, for potassium hydroxide 2.00; diffusion coefficients: 1.08, 2.80, 3.30 sq. cm./day, respectively. Better values for the diffusion coefficients would be 0.90–0.95, 2.3–2.5 and 2.6–2.8, respectively. These values are important in establishing the relation between rate constants and diffusion coefficients in heterogeneous reactions, because they lie between the group of low values (mostly weak acids) and the group of high values (strong acids).[8]

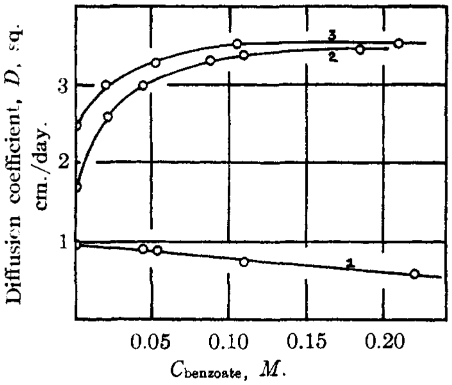

Fig. 1.—Effect of benzoate on the diffusion coefficients: 1, benzoic acid + sodium benzoate; 2, sodium hydroxide + sodium benzoate; 3, potassium hydroxide + potassium benzoate.

Summary

The dissolution rate of benzoic acid from rotating cylinders has been measured in water, in sodium and potassium hydroxide solutions, and in solutions of these bases containing dissolved sodium acetate.

A rate equation derived on the assumption that neutralization occurs within a diffusion layer has been shown to accord satisfactorily with the rates in these solutions. The rate constants obtained are also in satisfactory agreement with the rate constants for other diffusion-controlled heterogeneous reactions.

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