character of these soap systems. In comparing one of these systems, sodium stearate–*n*-heptane, with that employing a homologous solvent, cetane, as is used in the study of Doscher and Vold, one would expect a similar or an even greater resemblance. However, inspection shows that these two systems differ widely from each other, both qualitatively and quantitatively. One feature common to both sets of data is the observation of phase islands, although they, too, differ considerably in size and location in the heptane and in the cetane system. These phase islands are reminiscent of similar features observed in aqueous systems, and are correspondingly designated in analogy with these systems by Doscher and Vold.

In the course of a study of the system sodium stearate–cetane by various methods in these laboratories it was desired to resolve, if possible, the inconsistent character of the two published phase diagrams of the soap in paraffinic solvents. Certain concentrations of the sodium stearate–cetane system were studied in sealed capillaries by means of the polarizing microscope, and also by visual inspection of larger samples in sealed glass cells. Special care was taken in the preparation, purification, and drying of the sodium stearate, which is notoriously difficult to obtain pure and dry. By prolonged evacuation of the sample at 150 to 180° it was possible to obtain reproducible results in differential thermal analysis of the soap; thermal analysis is a sensitive criterion of purity of many organic compounds.

The samples were thoroughly mixed, heated well past their t_i-points, and slowly brought back to room temperature. The t_i-points were then observed as the temperature was raised, *i.e.*, as the system changed from anisotropic to isotropic under crossed polarizers. The rate of heating was usually about 0.5 to 1° per minute except when the temperature came within about 20° of the expected transition. Then the heating rate was reduced and the observation of the transition was made repeatedly, the temperature sometimes being kept almost constant for several hours to ensure equilibrium conditions. Mechanical mixing by means of a magnetic plunger was used during these observations. The change in the reverse direction, *i.e.*, isotropic to anisotropic, was found to give poor reproducibility because of supercooling. In spite of careful examination it was not possible to detect any indication of phase islands in our observations.

The t_i-points observed optically as described are given in the table, and it is apparent that our observations differ substantially from those of Smith as well as from those of Doscher and Vold. In general these values are higher than the corresponding values obtained by Doscher and Vold, as taken from their published phase diagram.[1] Only at the higher soap concentrations do their values seem to coincide with the values presented in this work. Our experience with the difficulties of drying and maintaining dry samples of sodium stearate leads us to the suggestion that small traces of water may have been present in the samples reported in the literature. The effect of water on depression of t_i-points is indeed remarkable; the addition of as little as 0.17% water was found to depress by 48° the t_i-point of the anhydrous sample containing 9% soap. In addition, visual study indicated a profound difference between samples with water and those without, in their appearance and behavior on heating.[4]

It is difficult for the present to answer the question whether the existence of phase islands, independent of the nature of the hydrocarbon component, is also traceable to the presence of water. The phase diagrams reported by Doscher and Vold and by Smith do bear a great resemblance to aqueous systems.

A more detailed paper on this subject, consisting chiefly of a study of this system by differential thermal analysis, is in preparation.

Our thanks are due Messrs. R. J. Moore and E. R. White of Shell Development for the preparation and purification of the organic compounds.

OPTICAL OBSERVATIONS OF THE t_i TEMPERATURES FOR THE SYSTEM SODIUM STEARATE–CETANE

Sodium stearate content, % wt.[a]	t_i, °C. This work	t_i, °C. Doscher and Vold	t_i, °C. H_2O added
2	167	167	
9	215	180	165 (0.17%)
18	220	182	
30	240	240	161 (1.66%)
50	248	249	226 (0.65%)
67	259	253	
71	255	255	
100	282	280	

[a] These values have been rounded off to the nearest integer and are within ±0.3% of the Na Stearate concentration.

Since the writing of this note, a paper by A. S. C. Lawrence[5] has lent support to the thesis that traces of water may have influenced the systems described.

---

[4] Ref. 1, p. 1.

[5] Lawrence, *J. Phys. Coll. Chem.*, **52**, 1504 (1948).

SHELL DEVELOPMENT COMPANY
EMERYVILLE, CALIF.
RECEIVED SEPTEMBER 28, 1949

The Reduction of Bromic Acid by Hydrobromic Acid in the Presence of Hydrogen Peroxide

BY H. A. YOUNG

The net reaction for the reduction of bromic acid by hydrogen peroxide may be written[1]

$$BrO_3^- + 3H_2O_2 = 3O_2 + Br^- + H_2O \qquad (1)$$

Bray and Davis also concluded that the rate of the reaction could be expressed as the sum of two terms, the more important of which, after some

---

[1] Bray and Davis, THIS JOURNAL, **52**, 1427 (1930).

bromide ion had been formed, represents the rate of the reduction of bromic acid by hydrobromic acid. This conclusion was later substantiated by Young and Bray[2] who showed in addition that at values of hydrogen ion concentration above 0.3 N appreciable amounts of bromine accumulated in the reaction mixture. These authors concluded from rough measurements of the accumulated bromine that hydrogen peroxide was the reducing agent which was effective in removing the products of the reduction of bromic acid by hydrobromic acid. They postulated the following reaction scheme

$$BrO_3^- + H_2O_2 + H^+ \longrightarrow O_2 + HBrO_2 + H_2O \text{ (slow)} \quad \text{(a)}$$

$$BrO_3^- + Br^- + 2H^+ \longrightarrow HBrO + HBrO_2 \text{ (or } H_2Br_2O_3\text{)(rate determining)} \quad \text{(b)}$$

$$HBrO_2 + H_2O_2 \longrightarrow O_2 + HBrO + H_2O \text{ (rapid)} \quad \text{(c)}$$

$$HBrO + H_2O_2 \longrightarrow O_2 + H^+ + Br^- + H_2O \text{ (rapid)} \quad \text{(d)}$$

$$HBrO + H^+ + Br^- \rightleftarrows Br_2 + H_2O \text{ (very rapid)}$$

The present investigation was undertaken in an effort to obtain more reliable measurements of the accumulated bromine than those reported earlier.[2]

Each of the experiments reported in the present work was performed in the presence of 0.500 M perchloric acid and was done in duplicate. In one part, the bromine and tri-bromide ion concentrations were followed by means of a Beckman spectrophotometer in which the observation cell was maintained at 25°. All light intensity measurements were made at a wave length of 4000 Å., using experimentally determined values of 194 and 480 for the extinction coefficients of bromine and tribromide ion, respectively. In the duplicate, the evolved oxygen was measured as a function of the time with the usual gas evolution equipment. These experiments indicated also that the over-all reaction could be represented by equation 1, since the amount of evolved oxygen was always within two per cent. of the calculated amount. Since there was an inevitable error in the zero reading this deviation is of little significance. Values of dO_2/dt were obtained by taking tangents to the oxygen–time curve.

If A, B and C are used to designate the initial concentrations of bromate ion, bromide ion and hydrogen ion, respectively, and X is the change in hydrogen peroxide at any time t (*i.e.* X = 4 times the moles of O_2 produced, since a volume of 250 cc. of solution was used), the following equations obtain

$$d = 194(Br_2) + 480(Br_3^-)$$

$$(BrO_3^-) + 2(Br_2) + 3(Br_3^-) + (Br^-) = A + B$$

$$(Br_2)(Br^-)/(Br_3^-) = 0.0588$$

$$(Br^-) = B + \frac{X}{3} - \frac{5}{3}(Br_2) - \frac{8}{3}(Br_3^-)$$

$$(H^+) = 0.500 - 2\Sigma\,(Br_2)$$

From these relations it is possible to calculate the concentrations of the various molecular species at any time t in terms of the measured quantities X and d. Finally the concentration of HBrO may be obtained from the assumption that the hydrolysis of bromine is always established. From these concentrations the rates of evolution of oxygen from reactions d and c were obtained from the relations $V_c = (140/4)(H^+)^2(BrO_3^-)(Br^-)$ and $V_d = (3.5 \times 10^4/4)(HBrO)(H_2O_2)$. The value of k_c was taken from the earlier work and that of k_d was determined experimentally.[3]

Four pairs of experiments are reported in which the initial hydrogen ion and bromate ion (from potassium bromate) concentrations were kept constant at 0.500 and 0.005 M, respectively, the initial hydrogen peroxide was in large excess and kept nearly constant, and the initial bromide ion concentration varied from 0.0156 M to zero by the addition of different amounts of sodium bromide.

Calculated values of the concentration of bromine, hydrobromous acid, V_c and V_d, together with the observed values of dO_2/dt are listed in Table I for experiment 2.

TABLE I

EXPERIMENT 2

Time,	O_2, cc.	d	(Br_2), moles/liter $\times 10^3$	(HBrO), moles/liter $\times 10^9$	V_c $\times 10^4$	V_d $\times 10^4$	dO_2/dt obs. $\times 10^4$
0			0	0	0	0	0
4	19.2	0.590	2.60	7.61	1.05	3.2	2.8
5	26.0	.610	2.67	7.41	0.96	3.0	2.8
7	39.7	.605	2.57	5.99	.85	2.4	2.5
9	51.0	.593	2.46	4.99	.69	2.0	2.1
11	60.5	.557	2.25	3.99	.54	1.5	1.8
13	68.5	.505	1.98	3.09	.39	1.2	1.4
15	74.6	.440	1.68	2.35	.28	0.88	1.1
17	79.5	.376	1.40	1.79	.18	.66	0.88
19	83.3	.312	1.14	1.35	.11	.49	.67
21	86.2	.253	0.91	1.01	.05	.36	.54
23	88.5	.203	.72	0.76	0	.27	.42
25	90.4	.162	.56	.58	0	.21	.32
27	91.8	.127	.44	.43	0	.16	.26
29	92.9	.098	.34	.33	0	.12	.20
31	93.7	.076	.26	.25	0	.09	.15

By comparison of the last two columns of Table I, it becomes obvious that the rate of evolution of oxygen is fairly well represented by reaction d, and that under these experimental conditions reaction c (column 4) is not necessary. To a time up to about nine minutes, the agreement between the values in the last two columns is quite satisfactory; during the latter part of the experiment the accumulated error due to bromine volatilization would be expected to manifest itself in a calculated rate which is too slow.

---

[2] Young and Bray, THIS JOURNAL, **54**, 4284 (1932).

[3] A spectrophotometric investigation of the rate of the reaction between Br_2 and H_2O_2 in the presence of 0.500 M $HClO_4$ yielded a value of 3.5×10^6 for the specific rate of the reaction $HBrO + H_2O_2 = H^+ + Br^- + H_2O + \frac{1}{2}O_2$. This value is in agreement with the values given by Bray and Davis, THIS JOURNAL, **50**, 1654 (1928).

TABLE II

EXPERIMENTAL RESULTS

Initial concentrations: $HClO_4$, 0.500 *M;* $KBrO_3$, 0.00500 *M*

Experiment	1	2	3	5
Init. $[H_2O_2]$, mole/liter $\times 10^2$	4.86	4.81	4.56	5.63
Init. [NaBr], mole/liter $\times 10^3$	15.6	7.80	3.90	0
Max. (HBrO), mole/liter $\times 10^9$	6.75	7.6	5.1	2.1
$[Br^-]$, mole/liter at HBrO max. $\times 10^3$	7.6	4.0	2.6	1.5
Time, min., at HBrO max.	3	4	4	27
V_c for HBrO max. $\times \cdot 10^4$	1.7	0.96	0.88	0.39
V_d for HBrO max. $\times 10^4$	2.8	3.2	2.0	0.89
$d[O_2]/dt$ at HBrO max. $\times 10^4$	2.6	2.8	2.0	1.5

In Table II are given the results of three other sets of experiments. It will be observed from columns 7, 8, 9, of this table, that when the maximum value of hypobromous acid is reached early in the experiment (where the loss in bromine has been negligible and consequently the measurements are reliable) the rate of oxygen evolution can be represented by reaction d. Since it is not necessary to assume oxygen evolution by reaction c, these results seem to indicate that the rate of the reduction of $HBrO_2$ by Br^- in these strongly acid solutions is considerably greater than the rate of reaction c. It appears, therefore, that in solutions in which the bromide ion concentration is at least 2.6×10^{-3} *M*, reaction c should be replaced by a new reaction $HBrO_2 + H^+ + Br^- = 2\ HBrO$.

In the case of experiment 5, the results are inconclusive. The observed rate is greater than the rate of reaction d, and the indications are that in these concentrations reaction c must be considered also. Unfortunately, however, the accumulated bromine was not appreciable in this experiment until the experiment was well advanced, and conditions were such that the experimental error was relatively high.

DIVISION OF CHEMISTRY, COLLEGE OF AGRICULTURE
UNIVERSITY OF CALIFORNIA
DAVIS, CALIFORNIA
RECEIVED NOVEMBER 11, 1949

NEW COMPOUNDS

The Acylation of Biphenyl with Dimethylcarbamyl Chloride

Biphenyl has been acylated with dimethylcarbamyl chloride in the Friedel–Crafts manner, without a solvent. Both the mono- and the diamide were obtained.

4-Biphenyl-N,N-dimethylcarboxamide.—Into a 2-l., 3-necked flask equipped with a condenser, mechanical stirrer, thermometer and a Glascol heater were placed 600 g. (3.9 moles) of biphenyl and 325 g. (3 moles) of dimethylcarbamyl chloride.[1] During twenty minutes 400 g. (3 moles) of anhydrous aluminum chloride was added in 50-g. portions, at such a rate that the reaction temperature did not exceed 120°. After all of the aluminum chloride had been added, the temperature was raised slowly to 150–170° and maintained in that range for four and one-half hours. The resulting mixture was cooled and poured onto ice. The unreacted biphenyl (146 g., 24.3% recovery) was removed by distillation, and the residue was recrystallized once from methanol to give 566 g. of amide, m. p. 93–96°, 84% based on dimethylcarbamyl chloride. The amide could also be purified by distillation at 175–180° (1 mm.). After further crystallization from methanol the compound melted at 105.5–106.5° cor.

Anal.[2] Calcd. for $C_{15}H_{15}ON$: N, 6.22. Found: N, 6.21, 6.36.

The amide was treated for six hours with sodium hydroxide in boiling methanol, and the salt was refluxed for five minutes with 20% sulfuric acid to give biphenyl-4-carboxylic acid, m. p. 226.5–228° cor. Gull and Turner[3] reported m. p. 228° for this compound.

Previously described Friedel–Crafts acylations with carbamyl chlorides have been limited to the use of carbamyl chloride itself,[4] and diphenylcarbamyl chloride.[5] Other mention was made of the use of disubstituted carbamyl chlorides, but no experimental data were given for such a reaction.[6]

4,4′-Biphenyl-N,N,N′,N′-tetramethyldicarboxamide.—The procedure was the same as that used for the monoamide, except that the reaction was carried out for nine hours at 150–180°. The resulting mixture was decomposed by pouring into hot water, and the product was recrystallized from benzene. From 308 g. (2 moles) of biphenyl, 535 g. (5 moles) of dimethylcarbamyl chloride and 668 g. (5 moles) of aluminum chloride there was obtained 350 g. of diamide, m. p. 187–205°, 59% based on biphenyl. Further recrystallizations gave m. p. 217–217.5° cor.

Anal.[2] Calcd. for $C_{18}H_{20}O_2N_2$: N, 9.45. Found: N, 9.40, 9.45.

When the reaction mixture was decomposed with ice and dried, an infusible, methanol-insoluble product containing 4.3% aluminum and 6.1% chlorine[2] was obtained. The use of hot water in the decomposition freed the amide of aluminum compounds.

Hydrolysis of the amide with sodium hydroxide in boiling amyl alcohol followed by acidification gave an acid which did not melt or sublime and was insoluble in the usual organic solvents. These characteristics have been reported for biphenyl 4,4′-dicarboxylic acid.[7]

---

[1] Slocombe, Hardy, Saunders and Jenkins, THIS JOURNAL, **72**, 1888 (1950).

[2] The authors wish to thank Mr. W. B. Dunlap for these analyses.

[3] Gull and Turner, *J. Chem. Soc.*, 491 (1929).

[4] (a) Gattermann, *Ann.*, **244**, 30 (1888). Hopff and Ohlinger, "The Synthesis of Mono- and Dicarboxylic Acids from Aromatic Hydrocarbons and Carbamyl Chloride, with Special Consideration of Polycyclic Hydrocarbons," Off. Pub. Bd. Report P. B. 75249.

[5] Lellmann and Bonhoffer, *Ber.*, **20**, 2118 (1887).

[6] Hopff and Ohlinger, U. S. Patent 2,137,287; *C. A.*, **33**, 1759 (1939).

[7] Doebner, *Ber.*, **9**, 271 (1876).

RESEARCH LABORATORY
PHOSPHATE DIVISION
MONSANTO CHEMICAL COMPANY
ANNISTON, ALABAMA

J. H. SAUNDERS
R. J. SLOCOMBE
EDGAR E. HARDY

RECEIVED FEBRUARY 27, 1950

Tertiary Acetylenic Amines. II[1]

Parcell and Pollard reported a method for the synthesis of tertiary, acetylenic amines by the dehydrohalogenation of halo-alkenylamines with sodium amide in liquid ammonia.[2] The synthesis of 1-diethylaminopropyne-2 by

---

[1] This paper is abstracted from a portion of the Ph.D. Dissertation of R. F. Parcell, a project under the sponsorship of the Office of Naval Research.

[2] Parcell and Pollard, THIS JOURNAL, **72**, 2385 (1950).