$$N + NO = N_2 + O \qquad (IV)$$
$$N + NO_2 = 2NO \qquad (V)$$

The reaction

$$N + NO_2 = N_2 + O_2 \qquad (VI)$$

is probably much slower. As soon as oxygen atoms are present, reactions I and III will begin, of course. With an excess of nitrogen dioxide the reaction is undoubtedly completed in the gas phase, and an analysis of the contents of the liquid air trap gives some information as to the amount of nitrogen atoms present as well as the rate of the reaction. The data are given in Table II. The calculated percentage dissociation is based upon the assumption that reactions IV and V are the only reactions that are taking place.

Table II

Run	Total press.	Press. H_2O	Mole N_2	Mole NO_2 introduced	Mole NO formed	Percentage diss. N_2
1	0.44	0.002	0.013	0.00782	0.00086	1.7
2	.50	.013	.010	.00382	.00112	2.8
3	.37	.0	.015	0	.00008	0

Conditions for the Disappearance of the Afterglow.—If an excess of nitrogen dioxide is added to either the oxygen or nitrogen afterglow, the afterglow disappears, due to the removal of all active species, and nothing is left in the gas mixture except the oxides of nitrogen and the elementary molecules. As has been mentioned before, however, either of the oxides of nitrogen in certain small amounts will extinguish the nitrogen afterglow. Furthermore, a mixture of nitrogen and oxygen in certain definite amounts gives no afterglow. Nothing condenses out in the liquid air trap from this non-luminous mixture which shows the absence of nitrogen dioxide. Furthermore, nitric oxide and oxygen atoms cannot both be present, since these would react on the walls of the trap to form the dioxide. There is reason to believe that both oxygen and nitrogen atoms are present so that we may conclude that this non-luminous mixture contains no oxides of nitrogen, the oxides having been destroyed by reactions IV and V. Furthermore, if nitric oxide is added to this dark mixture, a strong afterglow is produced. This fact completes the argument that the oxygen afterglow is due to reaction III and that the "dark" mixture of oxygen and nitrogen contains no oxides of nitrogen as a result of reactions IV and V.

Summary

The reaction $NO_2 + O = NO + O_2$ has been estimated to have a probability of 10^{-5} per collision at 40°.

The reactions $N + NO_2 = 2NO$ and $N + NO = N_2 + O$ are shown to be fairly rapid reactions.

The reaction $NO + O = NO_2$ presumably takes place by triple collision, and is accompanied by the oxygen afterglow.

Urbana, Illinois Received June 10, 1935

[Contribution from the Department of Chemistry, University of Notre Dame]

The Electric Moments of Alkyl Borates and Substituted Boric Acids

By M. M. Otto

Several investigators[1] have found dioxane a very satisfactory solvent for use in the determination of the electric moments of compounds. Wilson and Wenzke[1d] found that dioxane has the property of dissociating the double fatty acid molecules into single ones. They obtained moments for acetic and propionic acid comparable with the moments obtained by Zahn[2] for the acid at temperatures high enough to warrant the complete dissociation into single molecules.

The moments of the substituted phenylboric acids were desired. As they are not soluble enough in benzene, dioxane, in which they are very readily soluble, was selected as the solvent. There might, however, be a complication factor due to the tendency of boron to coördinate with oxygen as indicated by Bowlus and Nieuwland.[3]

Phenylboric acid, *n*-amylboric acid and *n*-butylboric acid are soluble enough in benzene so that their electric moments might be measured in both solvents. It was also possible to measure *n*-amyl borate and *n*-butyl borate in benzene and dioxane. With these data it should be possible to decide the value of dioxane as a solvent for substituted boric acids.

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(1) (a) Williams, This Journal, **52**, 1831 (1930); (b) Williams, *ibid.*, **52**, 1838 (1930); (c) Smyth and Walls, *ibid.*, **53**, 2115 (1931); (d) Wilson and Wenzke, *J. Chem. Physics*, **2**, 546 (1934); (e) Kumler and Porter, This Journal, **56**, 2549 (1934).

(2) Zahn, *Phys. Rev.*, **37**, 1516 (1931).

(3) Bowlus and Nieuwland, This Journal, **53**, 3835 (1931).

Preparation of Compounds

The phenylboric acid, *n*-amylboric acid and *n*-butylboric acid were prepared from the appropriate Grignard reagent with *n*-butyl borate.[4] The phenylboric acid was crystallized three times from hot water and air dried. The *n*-amylboric acid and *n*-butylboric acid were crystallized once from hot water and twice from benzene. All of these compounds were stored in an empty desiccator in glass-stoppered bottles until used.

Distillation of a mixture, to remove the water formed, of either butyl or amyl alcohol and boric acid using a bead packed column gave either *n*-butyl borate or *n*-amyl borate.[5] These compounds were fractionally distilled through a good column with a minimum exposure to the moisture of the air, as they are readily hydrolyzed. The pure *n*-butyl borate had a density of 0.85349 and a refractive index for sodium D line of 1.40731, while *n*-amyl borate had a density of 0.85491 and a refractive index of 1.41826.

Apparatus and Measurements

The dielectric constants were determined by the method previously described[6] but using the variable oscillator diagrammed in Fig. 1. This oscillator may be obtained by modifying a commercial oscillator intended for radio service. The entire set is enclosed in a copper shield with the exception of the dielectric cell B and the precision condenser A. The stator of the precision condenser is connected to a copper shield enclosing the condenser. As may be seen by the diagram the two shields need only be connected together and then to the ground to constitute one side of the condenser tuning circuit. A short piece of wire enclosed in Pyrex tubing served as the other link between the precision condenser and the oscillator. With this arrangement a very stable oscillator free from body capacity results.

The UX134 frequency generator tube is used as a triode with the screen element serving as the true plate, the conventional plate serving as what might be called a pickup grid. This method is very satisfactory for safeguarding the oscillator from frequency change because of the load placed upon it when coupled to the radio circuit. To remove further this effect of load the oscillator was removed from the coupling circuit by means of a radio frequency amplifier.

To extend the accuracy of the measurement small fixed condensers, calibrated against the precision condenser, were inserted in series with the precision condenser and these two condensers connected in parallel with the dielectric cell. In this manner the entire range of the precision condenser was used for the measurements.

Density and refractive index were determined as in a previous article.[7] The polarization at infinite dilution (P_∞) was calculated by Hedestrand's formula[8] as described before.[9] The dielectric constant and density are recorded for solutions in benzene in Table I and for solutions in dioxane in Table II. The molecular refraction for phenylboric acid, *n*-amylboric acid and *n*-butylboric acid were calculated from measurements of solutions in dioxane. This should be permissible from the work of Allard and Wenzke.[10]

Discussion

There is a possibility that the boric acid may be associated in benzene as is acetic acid or that it may coördinate with the oxygen of dioxane. As dioxane[1d] has been shown to break up the complex double acetic acid molecules it may be assumed to act similarly with the boric acid if it is associated. Now if the moments of the boric acids are nearly the same in the two solvents, as they seem to be from Table III, then it might be concluded that phenylboric acid, *n*-amylboric acid and *n*-butylboric acid are not associated in benzene. The moments in the two solvents are not identical but the slightly lower moments in benzene might be due to the smaller concentrations permissible for that solvent.

Another explanation which might be formulated for the near identity of the moments in different solvents is that the acid forms with the dioxane a compound which has a lower moment and thus compensates for the raising of the moment by the breaking down of the complexes.

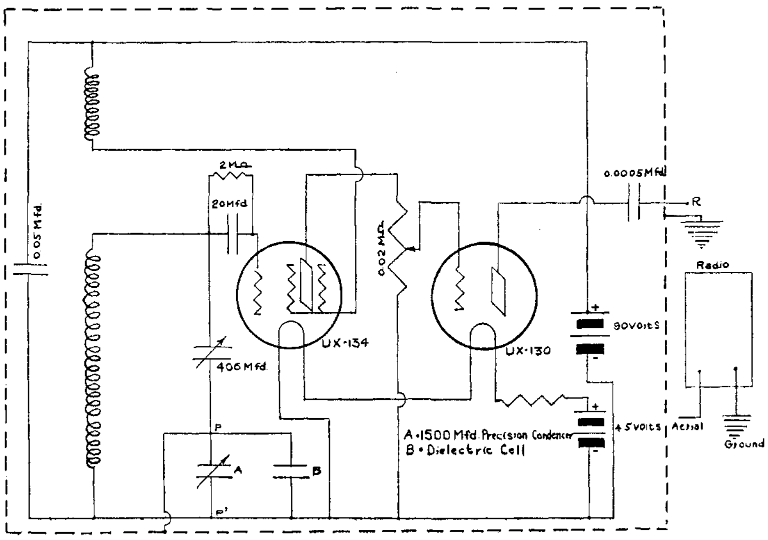

Fig. 1.—Diagram of variable oscillator.

Esters of boric acid would not be associated in benzene but there should be no reason why they

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[4] Bean and Johnson, THIS JOURNAL, **54**, 4415 (1932).

[5] "Organic Syntheses," John Wiley and Sons, New York, 1933, Vol. XIII, p. 16.

[6] Otto and Wenzke, *Ind. Eng. Chem., Anal. Ed.*, **6**, 187 (1934).

[7] Otto and Wenzke, THIS JOURNAL, **56**, 1314 (1934).

[8] Hedestrand, *Z. physik. Chem.*, **B2**, 428 (1929).

[9] Otto, THIS JOURNAL, **57**, 693 (1935).

[10] Allard and Wenzke, *ibid.*, **56**, 1693 (1934).

would not form compounds with dioxane as well as the substituted boric acid if such compounds are possible. Table III indicates that the moment in both solvents is approximately the same. This should be good evidence that there is no coordination between the boron and the oxygen of the boric acids and dioxane.

TABLE I

DIELECTRIC CONSTANTS AND DENSITIES OF SOLUTIONS IN BENZENE AT 25°

c_2	d^{25}	
	Butyl borate	
0.02236	0.87097	2.2722
.03221	.87023	2.2705
.03619	.86992	2.2701
.06479	.86779	2.2659
.08996	.86588	2.2605
	Amyl borate	
0.02891	0.87046	2.2681
.03944	.86959	2.2665
.05309	.86852	2.2644
.07106	.86717	2.2617
.09243	.86549	2.2593
	Butylboric acid	
0.001571	0.87153	2.2832
.001783	.87153	2.2844
.002074	.87154	2.2857
.002416	.87155	2.2872
.002969	.87155	2.2899
.003516	.87159	2.2924
.003819	.87161	2.2937
	Amylboric acid	
0.001977	0.87197	2.2858
.002858	.87196	2.2901
.003306	.87200	2.2922
.003769	.87200	2.2945
.004183	.87199	2.2965
.004516	.87201	2.2982
.006314	.87205	2.3068
	Phenylboric acid	
0.004606	0.87325	2.2938
.005270	.87339	2.2971
.006267	.87356	2.3005
.007021	.87391	2.3038
.007151	.87368	2.3042
.01188	.87505	2.3226

TABLE II

DIELECTRIC CONSTANTS AND DENSITIES OF SOLUTIONS IN DIOXANE AT 25°

c_2	d^{25}	
	Butyl borate	
0.00000	1.0283	2.3572
.02487	1.0151	2.3495
.03651	1.0089	2.3452
.04631	1.0036	2.3415
	Amyl borate	
0.00000	1.02834	2.3611
.05522	0.99584	2.3396
.07220	.98593	2.3318
.09169	.97435	2.3249
	Butylboric acid	
0.00000	1.02548	2.2405
.008080	1.02436	2.2845
.01293	1.02367	2.3097
.01616	1.02324	2.3292
	Amylboric acid	
0.00000	1.02544	2.2494
.008848	1.02402	2.2951
.01368	1.02303	2.3220
.01846	1.02219	2.3480
.02156	1.02239	2.3648
	Phenylboric acid	
0.00000	1.0283	2.3609
.01219	1.0299	2.4194
.01588	1.0306	2.4369
.01949	1.0319	2.4560

TABLE III

POLARIZATIONS AND ELECTRIC MOMENTS

Compound	P_∞ Benzene	P_∞ Dioxane	MR_D	$\mu \times 10^{18}$ Benzene	$\mu \times 10^{18}$ Dioxane
Butyl borate	78.77	79.44	66.34	0.77	0.79
Amyl borate	93.19	91.89	80.23	.79	.76
Butylboric acid	103.34	110.35	32.5[a]	1.85	1.94
Amylboric acid	111.67	112.68	36.8[a]	1.90	1.92
Phenylboric acid	91.94	98.28	36.4[a]	1.64	1.72

[a] Calculated from measurements of solutions in dioxane.

Because of its good solvent power for other substituted phenylboric acids which should act similarly to these here presented, dioxane should prove very useful in the determination of their moments.

Summary

1. Electric moments have been determined for butyl borate, amyl borate, phenylboric acid, *n*-amylboric acid and *n*-butylboric acid in benzene and dioxane solutions.

2. Evidence is offered for non-association of the above boric acids in benzene and for the lack of compound formation between dioxane and these acids.

3. Dioxane should serve as a good solvent for the determination of the moments of substituted phenylboric acids.

NOTRE DAME, IND.

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