solution; but it does show that we cannot compare the steric influence of two groups until we have studied the reaction in both acid and alkali. Thus the greater influence of the nitro than of the methyl group upon the esterification of the *ortho* substituted acids is due to the effect of the acid strength of the intermediate compounds with hydrogen ion, not, as has been often assumed, to a difference in mass; for we find a much greater rate of hydrolysis in alkali of the methyl *o*-nitrobenzoic than of the methyl substituent. Again the steric hindrance of a *meta*-nitro group is entirely explained by the above theory; in fact, the introduction of a nitro group in the *meta* position speeds up the hydrolysis in alkali more than it slows down the esterification in acid.

Summary

The rates and equilibria of the hydrolysis of methyl *o*-nitrobenzoate and methyl benzoate and the esterification of *o*-nitrobenzoic acid were studied under the same conditions: 60% methyl alcohol, 40% water, 0.25 *N* sulfuric acid, and 0.1104 moles per liter of organic acid or ester. It was found that (1) the equilibria for the substituted and unsubstituted bodies were practically the same; (2) the esterification reaction of the nitrobenzoic acid was found to be of a higher order than the corresponding hydrolysis; (3) the rate of hydrolysis of the nitrobenzoic ester was about $^1/_{20}$ as great as that of the benzoic ester. This last is contrary to the results obtained by Kellas working in alkaline solution. The discrepancy is explained by assuming the reaction to be preceded by complex formation between the ester and the hydrogen or hydroxyl ion. As may be expected, the nitro group favors the formation of the complex with hydroxyl ion and the dissociation of that with hydrogen ion, and consequently slows down the reactions in acid and speeds them up in alkaline solutions.

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A COMPARISON OF THE NORMAL BOILING TEMPERATURES OF UNDESICCATED SULFUR AS MEASURED BY THE DYNAMIC AND THE STATIC METHODS

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History and Outline of the Problem

Reference has been made elsewhere[1] to the literature of the extended controversy, particularly between Kahlbaum on the one hand and Ramsay and Young on the other, in regard to the identity of the boiling-point values obtained, respectively, by the static and the dynamic methods.

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[1] Compare Ostwald, "Lehrbuch der Allgemeinen Chemie," Engelmann, 1910, Vol. I, 308.

In 1910, by means of a form of apparatus especially well suited to the purpose, the present writer[2] was able to show that values identical at least to 0.01 mm. of mercury at 760 mm. pressure were obtained for the same temperature by the two methods in the cases of ethyl alcohol, water and benzene of the customary degree of impurity of purified specimens. In spite of the excellent concordance realized in these cases, there still remained, in the writer's mind, a doubt as to the facts in the case of sulfur. It is well known that the duplication of results in the employment of the sulfur boiling point as a standard temperature in thermometry requires careful attention to the conditions of experiment,[3] both as regards shielding of the thermometer bulb and in many other respects; but it appeared not impossible that some of the uncertainty of this boiling point might be due to a factor whose influence had apparently never been tested. The experiments here outlined were, therefore, undertaken to test whether the equilibrium between liquid sulfur freshly condensed from recently generated vapor occurs, for the same pressure near 760 mm., at the same temperature as that between liquid and vapor of greater age. The negative results then found might doubtless have been printed at that date,[4] over 12 years ago, but would then have had less significance to most readers than is to-day possible in the light of facts since brought forward by other workers.

The only investigators in this field who appear to have entertained even a suspicion of lack of constancy in the sulfur boiling point due to phenomena of metastability are Waidner and Burgess,[5] who write as follows: "It would seem that the only phenomenon that could cause this constancy to be questioned would be the existence of two forms of liquid sulfur of slightly different boiling points and one form gradually changing into the other with continued boiling. We have never been able to detect any such progressive change in the boiling point over several hours' time." It did not appear to the writer, however, that the rather leisurely type of change here suggested was the only possible one nor, indeed, the most probable one to which inconstancy might be attributable. For suppose, for example, that it were the case that the liquid freshly condensed on the thermometer bulb, where it remains for but a few seconds, should even in part go over within these few seconds to a liquid of different boiling point, then the boiling point observed would be a function of the average duration

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[2] Menzies, THIS JOURNAL, **32**, 1623 (1910).

[3] Compare Waidner and Burgess, *Bur. Standards Bull.*, **6**, 149 (1910).

[4] The results were announced orally by the writer to the Division of Inorganic and Physical Chemistry at the Minneapolis meeting of the American Chemical Society in 1910.

[5] Waidner and Burgess, *Bur. Standards Bull.*, **7**, 130 (1911). The reprint of their paper issued under date Dec. 6, 1910, became available only after the completion of the experimental work here described.

of sojourn of the molten condensed sulfur upon the thermometer bulb. It seemed of interest, therefore, to make boiling-point measurements on the same sample of sulfur with the same thermometer using (a) the dynamic and (b) the static method.

Experimental Part

The sulfur was obtained by fractional precipitation by hydrochloric acid from the aqueous solution of an excellent quality of recrystallized sodium thiosulfate. The middle fraction of the precipitate was distilled 5 times in sequence from as many distillation flasks previously blown together in series. The sulfur was not intensively desiccated.

The platinum-resistance thermometer was of the type in which the helical resistance wire is fused within a cylindrical bulb of quartz glass, 6 mm. in diameter and 60 mm. in length. It is unnecessary to detail the experimental arrangements for measuring resistance, since systematic error from this source would affect results by static and dynamic methods alike. Due correction was applied for the very small change in the constant of the thermometer that occurred during the work. Differences of temperature of 0.01° at 450° could be detected with ease. Pressure measurements were comparable within 0.2 mm. of mercury.

a. For the dynamic method, the thermometer bulb was adequately screened by a cone of asbestos paper tied above at its apex to the thermometer with asbestos cord, in order to secure the essential umbrella effect.[6] The glass boiling tube containing the sulfur was closely embraced by a cylindrical resistance furnace, serving as an insulating jacket, which was maintained at 250°, while the projecting lower closed end was heated by gas. All the precautions were observed which have since been summarized in their proposed standardization of the sulfur boiling point by Mueller and Burgess.[6]

b. For the static method, the static isoteniscope[7] was employed, and this was submerged in a transparent bath of fused nitrates, whose great heat capacity and high thermal conductivity rendered the thermometry simple, and special shielding of the thermometer bulb unnecessary. In the isoteniscope, the same specimen of sulfur remained for periods of minutes with a quiet surface in contact with the same specimen of vapor, except for the kinetic molecular interchange between vapor and liquid.[8]

When corrected[9] to 760 mm., the boiling-point values obtained by the

[6] Mueller and Burgess, THIS JOURNAL, **41,** 745 (1919), have since shown that this method of shielding is adequate.

[7] Smith and Menzies, *ibid.*, **32,** 1412 (1910).

[8] Van der Lingen and Wood, *Astrophys. J.*, **54,** 149 (1921). In the work of these authors with mercury, the vapor so situated in equilibrium with the liquid at constant temperature showed the phenomena of a "stagnant" vapor.

[9] The equation of Holborn and Henning, *Ann. Physik,* **26,** 833 (1908), was employed for this purpose.

dynamic and static methods did not differ by more than 0.02°, which was not outside the estimated error of experiment.

Reproducibility of the sulfur boiling point by the dynamic method has been attained as the result of the cumulative study of experimental precautions by many successive investigators. Quite aside, therefore, from deciding the point at issue, this result is of interest as demonstrating that the same temperature obtained by the much worked-over dynamic method is found by an independent static method, and at the first trial. Other things being equal, this would point to a greater sureness of simplicity of the static method here employed.

Discussion

That it was not entirely superfluous to look for a difference of boiling temperature where, in this instance, none was found, may become apparent from a consideration of the innocuous proposition that, in a given environment, *delay may occur before a new phase, freshly formed, reaches its equilibrium constitution and properties*, a statement that is reminiscent of the so-called law of successive reactions. It is evident that, if the delay be of short enough duration, no abnormal behavior will be observable. We are here concerned with freshly formed liquid and gas phases. Examples may, therefore, appropriately be limited to the change with time of the properties of (a) liquids freshly formed by the condensation of vapors, and (b) vapors freshly formed from an evaporating liquid.

a. It may be recalled that Smith and the present writer published,[10] in 1911, their curious observation that adequately desiccated calomel is without appreciable vapor pressure at 352°, a temperature at which ordinary, undesiccated, calomel shows a vapor pressure of about 350 mm. of mercury. This result was communicated privately to Professor Brereton Baker, who thereupon searched his own laboratory records for similar phenomena and was rewarded by unearthing the cases of nitrogen trioxide and tetroxide.[11] He then set up many similar desiccation experiments, which lay dormant during the war, and has recently announced some of his findings.[12] In the case of intensively desiccated benzene, for example, the liquid boiled at 106°, while a thermometer in the condensing vapor registered 80°. The distillate, however, boiled at 105°. From this it is evident that, while the vapor condenses at first to a liquid of apparently normal behavior, this liquid soon reverts to the abnormal condition of high boiling point. While it is true that the benzene had been subjected to rather unusual treatment, it is also true that the effect of this treatment was a change in boiling point of surprising magnitude. Changes

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[10] Smith and Menzies, *Z. physik. Chem.*, **76**, 713 (1911).

[11] Baker, *J. Chem. Soc.*, **101**, 2339 (1912).

[12] Baker, *ibid.*, **121**, 568 (1922).

of the same character, if of smaller magnitude, might not unreasonably be expected in liquids less drastically treated, a matter which is being investigated in this Laboratory.

Some insight into the mechanism of an action which is hindered by the presence of traces of water, namely, the production of diatomic from monatomic hydrogen, may be gained from a study of the work of Wood.[13] Here, also, the presence of water hinders molecular growth, as it appears to do in the case of calomel and the substances studied by Baker.

b. As an example of rapid change in the properties of a freshly generated vapor, one may recall the observations of Van der Lingen and Wood on the fluorescence of mercury vapor.[8] These skilful experimenters demonstrated that only the freshly generated vapor from mercury exhibits fluorescence. The quiescent or stagnant vapor does not. Stated otherwise, evaporating mercury yields a vapor containing active molecules which shortly become passive with respect to fluorescence. The facts are similar also for resonance phenomena.

Working in a different field, Karl Compton and Yao[14] find that a markedly lower voltage is required to strike an arc in mercury vapor between electrodes close to the liquid mercury surface than between electrodes farther removed from this surface, which may be considered as a source of vapor molecules of comparatively recent origin.

Turning to another case, that is perhaps less unequivocal, we find Baly and Duncan[15] by rapid evaporation of liquid ammonia obtaining an "inactive" variety of ammonia gas which reverts, on standing for hours in contact with the liquid, to the normally active variety. This experimental result is equally instructive whether or not the phenomenon be sulfur due to the presence of other substances.

Summary

It has been shown experimentally that identical results are obtained for the boiling point of undesiccated sulfur whether the dynamic or the static method be used. It is suggested that this might not be so if they were, accidentally or intentionally, desiccated.

The statement that delay may occur before a new phase, freshly formed, reaches its equilibrium constitution and properties, is examined for the cases of certain liquids and vapors.

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[13] Wood, *Phil. Mag.*, **44**, 538 (1922).

[14] I am indebted to my colleague, Mr. Compton, for permission to report here this observation, an account of which will appear in *The Physical Review*.

[15] Baly and Duncan, *J. Chem. Soc.*, 121, 1008 (1922).