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REACTIONS OF ANESTHETIC ETHERS WITH POTASSIUM HYDROXIDE AND WITH MERCURY AND THE TEST FOR FOREIGN ODORS

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Experience over a long period of years in the testing of ether has enabled us to interpret, with at least a fair degree of accuracy, the meaning of the various appearances that arise when ethers of different compositions and purity are tested for aldehyde with potassium hydroxide. In the hope of establishing a more complete understanding of this test, our conclusions and a few typical experiments are given in the following pages, together with some remarks on the action of mercury on ether containing peroxides and the results obtained by the application of the test for foreign odors to many cans of old anesthetic ether.

The U. S. Pharmacopœia (X edition) requires that no coloration shall develop within two hours when 10 cc. of ether is mixed with 1 cc. of potassium hydroxide test solution and occasionally shaken.

By breaking weighed, sealed glass bulbs of pure aldehyde under pure ether, three ethers were prepared containing, respectively, 0.025 g., 0.05 g. and 0.075 g. of aldehyde per 100 g. of ether.

By holding the test-tubes before a sheet of white paper, one observer detected a pale yellow color with ether containing 0.05% of aldehyde but could find no color with 0.02%. An observer making the test for the first time detected 0.1% of aldehyde but could detect no color with 0.05% after one hour. After several hours, however, he could detect the color. Another observer was able to detect 0.025% of aldehyde readily if care was used, but got no reaction with 0.0125%. A 5% potassium hydroxide solution was used as directed in U. S. P. VIII. Recently another trial has been made by entirely different observers using 5.6% potassium hydroxide (*N*) as directed by U. S. P. X. A solution of acetaldehyde in pure aldehyde-free ether was prepared and its aldehyde content accurately determined by titration. This solution was then diluted with pure aldehyde-free ether, making known aldehyde solutions of 0.005, 0.01, 0.02, 0.04 and 0.06% acetaldehyde. It was found that the temperature at which the test was made had quite a pronounced effect upon the minimum amount which could be detected. By holding the tubes in a good light, using a white paper background and comparing the color with a blank, using pure distilled water in the place of potassium hydroxide solution, and covering this with a layer of ether, the minimum amount which could be detected was 0.02% at 35°, while at 15° it required 0.04% to give a corresponding color. This places the maximum sensibility of the test under ideal conditions at 0.03%, making the observation at average laboratory temperature of 25°. It is safe to say that under average conditions the limit of sensibility of this test would be in the neighborhood of 0.05 to 0.06%.

This test appears to be much less sensitive than the test of the German and Austrian Pharmacopœias employing solid potassium hydrate. The use of solid potassium hydrate is to be preferred to the solution as a reagent for aldehyde, both on account of greater sensitiveness and because, as will appear later, the various appearances around and on the surface of the lumps of potash give valuable indications as to the presence of alcohol and peroxides in the ether. We have never employed this test except to determine its sensitiveness in the above experiments.

The German Pharmacopœia (Ph. G. VI) requires that anesthetic ether (*aether pro narcosi*), when placed in a glass-stoppered bottle protected from the light, shall not become colored itself and shall not impart any color, after six hours, to freshly broken lumps of potassium hydroxide the size of a pea. Following the German procedure, 30 cc. of ether and 5 g. of fresh pure potassium hydroxide sticks were used in each test.

Baskerville[1] states that anhydrous ether should give no response in this test for twenty-four hours. It should be noted, however, that this reaction in the complete absence of water is not to be depended upon to indicate aldehyde, as the following experiments indicate.

Aldehyde Can Produce No Color in the Absence of Water

It was soon observed in applying this test to pure anhydrous ether containing 0.1% of pure acetaldehyde that the characteristic brown coloration tended to make its appearance on the curved surfaces of the fragments of potassium hydroxide sticks and not on the freshly broken surfaces. By sandpapering off the cylindrical surface, that surface lost its property of acquiring the brown color, behaving then like the freshly broken surfaces. By holding the sandpapered stick of potassium hydroxide in a steam jet for a few seconds and making the test with it, the coloration reappeared on the sandpapered surface, showing that the presence of a slight amount of moisture in the potash is necessary for the proper formation of the color.

It was thought that a trace of carbonate in the crust on the caustic sticks might be one of the causes of the coloration appearing on the cylindrical surfaces. Accordingly, a test was made using instead of potassium hydroxide, potassium carbonate containing about one and one-half molecules of water, and another test after drying the potassium carbonate at 120°. The ether used contained, besides traces of alcohol and water, sufficient aldehyde to color potassium hydroxide a good brown. After thirty-six hours under this ether, the potassium carbonate, both dried and undried, was uncolored. The ether was then poured from the potassium carbonate into bottles containing the usual 5g. portions of potassium hydroxide. The ether from the dried salt became strongly turbid at once and the pieces of potassium hydroxide after several hours acquired a pale yellowish-brown tint, whereas the ether from the undried potassium carbonate colored the potassium hydroxide a deep brown.

Evidently potassium carbonate, while it plays no part in the production of the color on the lumps of potassium hydroxide, is able to dry ether containing considerable aldehyde to the point where the potassium hydroxide test fails to indicate the presence of aldehyde by the production of the usual brown color.

Sensitiveness of the Solid Potassium Hydroxide Test

Pure anhydrous ether free of aldehyde was prepared and determinate amounts of pure aldehyde were added corresponding to 0.025 g., 0.05 g. and 0.075 g. per 100 g. of

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[1] Baskerville and Hamor, *J. Ind. Eng. Chem.*, **3**, 396 (1911).

ether. The best way to prepare such determinate solutions is by weighing pure aldehyde in small, sealed glass bulbs and breaking them under ether. Our solutions were prepared in this manner. Thirty cc. of these ethers were poured upon 5 g. of freshly-broken sticks of potassium hydroxide in glass-stoppered bottles. Duplicate bottles were made and placed in light-tight cases to test the effect of excluding the light as required in the above mentioned Pharmacopœia. It was found necessary to reject the first set of tests, for there was so little moisture present that at the end of three hours the potash was still white, even in the ether containing 0.075 % of aldehyde. A large drop of water was now added to the bottle containing the ether with 0.075% of aldehyde and in twenty-five minutes the potash became distinctly brown, thus showing the remarkable part played by water in facilitating the reaction between aldehyde and alkali. Four fresh tests were prepared, one with the pure ether and three with the ether containing the aldehyde, and to each test was added one drop (about 0.04 cc.) of water. A set of four duplicates was placed in the dark. The ethers containing 0.075% and 0.05% of aldehyde began to show perceptible color in about fifteen minutes, the tests protected from the light showing a slightly deeper tint. At the end of two hours, the ether containing 0.02% of aldehyde had produced a good brown on the potash and the ether itself was a pale amber color. This sample was overlooked at the end of the first hour, but had it been observed, it is probable that the color could easily have been detected. However, the full depth of the brown does not appear until from two to four hours have elapsed and, with very small amounts of aldehyde, twelve hours may be required for maximum color. The pure ether used for making these solutions gave absolutely no reaction even after several days.[2] A comparison of the tests which had been protected from the light with those exposed to the ordinary daylight showed no marked difference. At the end of five hours, however, it was just possible to distinguish by their slightly darker tints the bottles which had been kept in the dark. It would seem that the importance of protecting the tests from light has been overestimated. We have observed some slight influence from light in other experiments, but we have not ascertained the exact nature of the effect. For extreme delicacy the exclusion of light is perhaps desirable.

Further experiments showed that this test will detect 0.01% of aldehyde in pure ether. The observer should familiarize himself with the indications of the test by comparing pure ether with ether containing known amounts of pure aldehyde. The test fails absolutely to give reliable indications at dilutions of 0.001% of aldehyde, although we made many attempts to increase its sensitiveness. Possibly some indications may be obtained with less than 0.01% of aldehyde, but below this limit we prefer to employ other reagents of greater sensitiveness. As will appear later, this sensitiveness (0.01%), representing the limit for pure aldehyde in pure ether, cannot be attained in applying this test to ordinary ethers unless the proper amount of water is present to overcome the interference produced by the alcohol normally present in such ethers.

The Significance of Turbidity and Effect of Alcohol

Baskerville and others appear to regard the appearance of a turbidity in the potassium hydroxide test as indicative of the presence of aldehyde. "On covering 5 g. of solid potassium hydroxide in freshly broken pieces

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[2] This degree of purity is not difficult to obtain by laboratory methods. Compare Wobbe, *Apoth. Ztg.*, **18**, 466 (1903).

about 5 mm. in diameter with 30 cc. of the sample and allowing to stand for six hours tightly closed and protected from light and occasionally shaking, the potassium hydroxide should not acquire a yellowish color, no yellowish or brownish-colored substance should separate and *the ether should not become turbid* or assume any color."[3]

The quotation appears ambiguous as to whether an ether which becomes turbid immediately and then clears up after several hours would be construed to have passed or to have failed. Presumably it would be held to have failed.

The absence of a turbidity, that is, the ether remaining water-clear in the potassium hydroxide test, seems to depend upon too many factors to be relied upon as a proof of the purity of ether. As the following tests indicate, the amount of alcohol present influences this largely, ethers rich in alcohol but perfectly pure and normal otherwise generally produce a turbidity which clears up more or less after several hours.

Twenty cubic centimeters of ether free from aldehyde and dehydrated over metallic sodium, to which had been added 0.72 cc. of absolute alcohol and 0.08 cc. of water to imitate the composition of anesthetic ether required by the U. S. Pharmacopœia (9th Edition now superseded by 10th), produced an immediate turbidity when poured upon the caustic. The aldehyde introduced by the alcohol is trifling. We have seen many specimens of ether of 0.711 sp. gr. (water and ether at 25°) which were sufficiently free from aldehyde to give to potassium hydroxide no color for eighteen hours and yet if several per cent. of "Cologne Spirits," which contains less aldehyde than the ordinary grain alcohol, were added to the ether, an immediate turbidity, when poured on the potash, would result.

To further demonstrate the influence of alcohol on the reaction, two aldehyde tests were made on a pure aldehyde-free ether containing about 3% of cologne spirits and to one of the test bottles two drops of water were added. After standing some twenty hours, the test without water was still slightly turbid and the potash showed a yellowish coloration, whereas the test containing water showed no turbidity and the potash remained white. It is evident that the turbidity and also the formation of a coloration which might easily be mistaken for a trace of aldehyde in the ether, is due to the alcohol. That the presence of alcohol interferes with the detection of aldehyde was known to Vulpius[4] and confirmed by Schobig,[5] who pointed out that ether containing several per cent. of alcohol dissolved 40 mg.[6] of potassium hydroxide in 10 cc. and likewise tended to dissolve aldehyde resin, as shown by the yellow color of the ether.

We have repeated many times the experiment of adding several per cent. of cologne spirits to ethers in which the potassium hydroxide would remain almost, but not absolutely, snow-white for several days and always with the same general result, namely, more or less coloration at the end of about twenty-four hours upon the caustic and the production of a yellowish or brownish sediment. This deposit sometimes takes the form of

[3] Ref. 1, p. 393.

[4] Vulpius, *Apoth. Ztg.*, **9**, 7 (1894).

[5] Schobig, *ibid.*, **22**, 210 (1894).

[6] We found similar amounts dissolved by ether containing 4% of absolute alcohol.

feathery crystals several millimeters in length adhering to the lumps of potassium hydroxide. Whether or not one is prepared to admit the similarity between the shade of color produced by alcohol and that produced by aldehyde, the fact remains that alcohol greatly modifies the appearance of the test. The disturbance increases with increase in the amount of alcohol in the ether and the time of standing. When several per cent. of alcohol is present, twenty-four hours is too long to allow to stand before observation. Six hours is usually a safe time to allow for the aldehyde color to develop before the alcohol produces its yellow discoloration or feathery crystals, although tests will occasionally remain unharmed by the alcohol for twelve to eighteen hours.

We have stated that the presence of a certain amount of water in an ether containing several per cent. of alcohol helps to overcome the effect produced by alcohol in the potassium hydroxide test. In order to determine whether the sensitiveness of the test is diminished by the presence of water, and also the proper way to add the water, tests were made with fresh potassium hydroxide unexposed to moisture and with the same after it had stood overnight over water in a desiccator, and by a third procedure which consisted in adding a few drops of water to 30 cc. of the ether to be tested, shaking vigorously and then pouring the moistened ether over fresh potassium hydroxide. Four ethers of different composition were used, as follows.

Ether (1) was pure anhydrous ether containing 0.01% of aldehyde. It produced absolutely no color on unmoistened potassium hydroxide even for forty-eight hours, but the potassium hydroxide exposed to moist air showed a distinct brown in six hours. Ether (1) shaken with three drops of water did not produce as distinct a brown as the potassium hydroxide exposed to moist air, but it was still detectable.

Ether (2) was pure anhydrous ether containing 1.42% of absolute alcohol and was intended to show the disturbing effect of alcohol. With *unmoistened* potassium hydroxide, after six hours, this ether became turbid and yellowish and some precipitate formed, although the potassium hydroxide remained white. After twenty-four hours the color deepened and the potassium hydroxide appeared partially dissolved. Test valueless. In sharp contrast to the above, the *moistened* potassium hydroxide showed only a slight haziness after six hours. Ether (2) shaken with three drops of water remained clear for twenty-four hours and the potassium hydroxide was white except for a few minute, brownish crystals starting to form, indicating that the alcohol was beginning to show its effect.

Ether (3) was pure anhydrous ether containing 1.28% of absolute alcohol and 0.01% of aldehyde, and was designed to show the combined influence of alcohol and the least amount of aldehyde that can be detected by this test. With *unmoistened* potassium hydroxide, the ether was yellow after six hours, but the potassium hydroxide showed no true brown color. Test valueless. *Moistened* potassium hydroxide, however, after six hours, showed a faint true brown color, but after twenty-four hours the test was valueless, due to the effect of the alcohol. When ether (3) was shaken with three drops of water, the potassium hydroxide showed a trace of true brown after six hours, and after twenty-four hours the potassium hydroxide showed a distinct true brown and the test was still free from alcoholic effect.

Ether (4) was a pure anesthetic ether containing about 0.25% of water and 0.33% of alcohol to which 0.01% of aldehyde was added. This was intended to represent ordinary anesthetic ether such as might be met with on the market. It was of special interest, therefore, to show whether the potassium hydroxide test would detect the aldehyde in it. Both unmoistened and moistened potassium hydroxide showed a true brown in six hours. When ether (4) was shaken with three drops of water, the color after six hours' standing upon the potassium hydroxide was not so strong, but after twenty-four hours the color was practically normal.

Reaction of Mercury with Ether Containing Peroxides

Before considering certain abnormal indications which arise when the potassium hydroxide test is applied to ether containing peroxides, we will refer to the following chance observation made thirteen years ago.

Four or five samples of an excellent grade of anesthetic ether, originally free from aldehyde, which had been kept in glass-stoppered bottles for about a year in a laboratory closet (only occasionally exposed to daylight), were found to be rich in peroxides, but when tested for aldehyde in the usual manner with potassium hydroxide, produced only a slight brown color.

Copious precipitates, some black and some light gray, resulted on shaking these samples with mercury and the aldehyde test applied as above now quickly showed the characteristic dark brown color on the potash. One sample became almost black, indicating the presence of aldehyde far in excess of that generally present even in commercial ethers. No intensified reaction could be obtained by shaking with mercury an ether rich in aldehyde (containing over 0.1%) but free from peroxides and no reaction whatever could be obtained from pure ether by such shaking. The reaction is very sensitive and an ether which gives an easily recognizable yellow with cadmium potassium iodide will also show, when carefully observed, a slight tarnishing or production of a skin on the bright surface of a globule of clean mercury. Ether which has been in contact with rubber will blacken mercury, although containing no peroxides. The color of the precipitate due to peroxides is generally grayish-black but may be light gray or, if water is present, it may be yellowish.

Although the peroxides present in the ether were completely destroyed after five hours shaking with mercury on a vigorous mechanical shaker, the weight of the powder, because of its variable composition, even after allowing for the finely-divided metallic mercury in it, cannot be taken as a measure of the active oxygen present. We were forced to abandon the idea of a quantitative method based upon this reaction. The precipitate is non-explosive, contains considerable acetic acid and the color can be made to vary by digestion with water.

The use of mercury for removing traces of peroxides in ether is well known,[7] but we have seen no reference to the simultaneous liberation of aldehyde. This reaction agrees with the results of Clover,[8] who proved that acetaldehyde was one of the main decomposition products of the organic peroxides in many old ethers. Warming ether containing peroxides with a few drops of 50% sulfuric acid will often liberate sufficient aldehyde to indicate itself by the potassium hydroxide test.

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[7] Bein, "Ausdehung des Aethylaethers, etc.," *Wissenschaftliche Abhandlung der Kaiserlichen Normal-Eichungs Kommission*, Heft VII, Metronom. Beitrage, p. 42.

[8] Clover, THIS JOURNAL, **44**, 1107 (1922).

Referring to the tarnishing of mercury by impure ether, Baskerville[9] says "that only the presence of free sulfur or hydrogen sulfide can produce the reaction generally ascribed to organic sulfur, excepting, of course, hydrogen dioxide which produces a gray precipitate even when present in mere traces." It is true that mercury is very easily corroded even by 0.001% of the *organic* peroxides naturally occurring in ether, but by pure hydrogen dioxide it appears to be but little attacked, as the following experiments show.

To two portions of pure ether showing no reaction either with cadmium potassium iodide or ammoniacal silver nitrate, aqueous hydrogen peroxide was added equivalent to 0.01% of H_2O_2 and 0.1% of H_2O_2, respectively. After shaking these two samples and also a comparison sample of pure ether for one hour with mercury, the mercury in the pure ether was only very slightly tarnished, the surface remaining bright except for a few separate specks; the ether containing 0.01% of H_2O_2 differed very slightly from the pure ether, the mercury containing a few more specks. The total tarnishing was insignificant in either. The ether containing 0.1% produced barely sufficient grayish powder to conceal the surface of the mercury, whereas ether containing 0.1% of the natural organic peroxides gives, as already stated, a copious precipitate. Other portions of each ether were allowed to stand for six days before shaking with mercury to test whether the mercury would then be greatly attacked, but the results were substantially the same. No hydrogen peroxide could be found in any of the samples after the shaking with mercury. Mercury is not very readily converted into the finely-divided metallic state by shaking with ether. After shaking the ether containing 0.1% of H_2O_2 with a weighed amount of mercury on a mechanical shaker for five hours, the loss of weight due to the formation of the powder which was separated from the globule before weighing amounted to less than 0.2 g. Another sample of ether containing 0.09% of H_2O_2, when shaken for five hours with 2 cc. of mercury, produced a small amount of yellowish powder insufficient to cover its surface.[10] After long contact with hydrogen peroxide, however, ether does acquire the property of readily corroding mercury, presumably because of the formation of organic peroxides as explained by Wieland and Wingler.[11]

The Effect of the Presence of Peroxides

Baskerville[3] states, as the result of his experiments, that "peroxides may cause a turbidity, but no coloration or colored separate." This is true, but this statement and the preceding paragraph should not be taken to mean that neither hydrogen peroxide nor the natural peroxides interferes with the detection of aldehyde by means of the potassium hydroxide test, as the following experiments indicate.

Ether containing about 0.15% of aldehyde was exposed to an ordinary glass mercury vapor light for sixty hours. A portion of the light-treated ether, which now gave a strong test for peroxides with the cadmium potassium iodide reagent, was shaken for five hours with metallic mercury to liberate the aldehyde. Comparative aldehyde tests

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[9] Ref. 1, p. 308.

[10] The well-known catalysis of hydrogen peroxide by mercury (Bredig and Weinmayr, *Z. physik. Chem.*, **42**, 601 (1903)) would lead one to expect some such results with ether.

[11] Wieland and Wingler, *Ann.*, **431**, 301 (1923).

were next made using both fresh caustic and caustic exposed to moist air on the original ether, on the light-treated ether and on the latter after shaking with mercury. The caustic in the light-treated ether was almost white, showing less color than is produced by 0.01% of aldehyde, and there was only a slight increase even after twenty-four hours' standing. The portion of light-treated ether shaken with mercury produced in four hours a notably darker color estimated to be at least equal to the presence of 0.03% of aldehyde and the color increased considerably after twenty hours. With original ether, the aldehyde was evident in five minutes and after four hours the caustic was strongly colored rusty brown and considerably darker than the ether which was shaken with mercury. Evidently the liberation of the aldehyde is not quantitative. Sunlight produced similar results. Exposure to ordinary daylight for several hours seems to be without injurious influence, but a half day's exposure has produced the effect.

Aqueous hydrogen peroxide was added to ether containing 0.1% of aldehyde in the proportion of two molecules for one of aldehyde and the solution was kept in the dark for three days and occasionally shaken.[12] An aldehyde test now showed a scarcely perceptible yellow color after one-half hour. The color deepened somewhat on long standing but the caustic assumed a yellowish color and powdery appearance. A portion of the original ether treated with peroxide was shaken with mercury and the test then showed a strong reaction after twenty minutes, thus proving that the aldehyde was not destroyed. These experiments suggest a possible explanation for the fact frequently observed by us that ether rich in the naturally occurring peroxides gives only a feeble aldehyde reaction (or even none at all) with potassium hydroxide, although the ether when fresh may have contained sufficient aldehyde to give a dark brown coloration. It is clear that hydrogen dioxide and likewise the peroxide naturally occurring in ether interfere greatly with the production of the characteristic dark brown color, rendering the test far less sensitive and indeed practically useless for indicating small traces of aldehyde.

Potassium Hydroxide Test Applied to Peroxidized Ethers

Most specimens of ether containing several per cent. of alcohol will give, when they have acquired sufficient peroxide, a marked turbidity which persists for many hours and finally settles out as a yellowish or brownish precipitate after from eight to twelve hours. The lumps of potassium hydroxide then appear to have been pitted or partially dissolved and the test has a characteristic appearance.

In the case of peroxidized ether which originally contained little or no alcohol, no turbidity is produced, the ether remaining water-clear and the lumps of caustic frequently exhibit a sort of blistered appearance and are only slightly colored, due presumably to the liberation of a little aldehyde from the peroxides. The following examination is intended to illustrate these conclusions and gives the results obtained by applying the potassium hydroxide test to a number of samples of ether which had stood in amber bottles tightly stoppered with corks on the laboratory shelf for about six months, including the heat of the summer. The ether was originally of good quality, sp. gr. $0.711\ \frac{25^\circ}{25^\circ}$ and practically free from aldehyde, and to a portion of it several per cent. of pure cologne spirits had been added. Almost all of the bottles had partially evaporated, many having lost one-

[12] From Wieland and Wingler's work this result might be expected. Ref. 11.

quarter of their contents. For purposes of comparison, samples which were free of peroxides were also tested.

Of thirteen samples of alcoholic ether giving marked peroxide tests, all gave a *marked turbidity* when poured upon the potassium hydroxide. After about five hours' standing, six of the tests were still turbid, resembling a solution containing freshly precipitated aluminum hydrate. Four were yellowish and the precipitate had settled. Of six comparison samples (free of peroxides) five gave a slight turbidity upon pouring upon the potassium hydroxide, and after about five hours five were *slightly* turbid, but *none showed a marked turbidity* resembling aluminum hydrate. After standing overnight, eleven of the tests on the peroxidized ether were brownish and the potassium hydroxide lumps appeared partially dissolved, while five of the peroxide-free ethers showed only pale yellowish sediments and no dissolving of the potassium hydroxide. Of seventeen samples of the non-alcoholic ether giving marked peroxide reactions, four showed a turbidity after the test had stood for five hours, the balance being clear; but in eleven of these the potassium hydroxide was yellowish and in eight the potassium hydroxide had a blistered appearance in addition to being colored. Four comparison samples (peroxide free) were all clear and the potassium hydroxide white in three and almost white in the fourth.

Anyone using the test with solid potassium hydroxide day in and day out on ethers of varying composition will be struck by the variations in the phenomena attending the test, and herein lies its chief defect, for the observer must make allowances for the disturbing influences caused by the presence in the ether of such common impurities as alcohol and peroxides. The pure brown coloration on the lumps of potash normally produced by pure aldehyde in pure ether may be obscured or replaced more or less by the other appearances which, while difficult to describe in an adequate manner, are readily recognized after having once been seen.

We may sum up briefly the results of all experiments with the potassium hydroxide test as ordinarily employed, using lumps of potash, as follows.

As a means of detecting aldehyde it is unreliable in the presence of peroxides unless these are present only in very small traces. Before applying the test, such ether may be shaken with mercury to liberate the aldehyde combined with the organic peroxides. However, what evidence we have indicates that this decomposition is not quantitative.

The appearance of a turbidity which remains undiminished in intensity for some hours points to an alcoholic ether containing considerable peroxides. Alcohol itself produces a turbidity which is not easy to distinguish from that due to peroxides. Contrary to the prevailing opinion, the appearance of a turbidity is in no way indicative of the presence of aldehyde and is an indication from which no positive conclusions can be drawn unless substantiated by other tests.

The test will not indicate aldehyde in the complete absence of water. The presence of several per cent. of alcohol in ether, especially if not accompanied by the usual amount of water, produces a coloration which resembles the aldehyde color. The use of potassium hydroxide which has been exposed to moist air will avoid the first difficulty, but to avoid the second it may be necessary to moisten the ether with water, three drops to 20 cc. If this is done, the effect of the alcohol which otherwise may manifest itself in several different appearances on the lumps of caustic is delayed for at least twelve to eighteen hours, amply sufficient to allow the aldehyde color to attain its maximum. While it is easy to detect 0.01% of aldehyde in pure ether, it requires some experience and the proper use of water to detect this amount in an alcoholic ether. Since many anesthetic ethers contain from 0.5 to 1% of water,[13] the use of potassium hydroxide exposed to moist air will suffice if fresh caustic fails to indicate aldehyde, but in the absence of any information concerning a given specimen three tests should be made: namely, with fresh caustic, with caustic which has been exposed to moist air and by using water in the ether itself.

When ether contains both alcohol, to the extent of several per cent., and considerable aldehyde, say 0.1%, there is generally formed a precipitate which resembles ferric hydrate both in form and color.

We have occasionally noticed a transient yellow color which appeared on the potassium hydroxide in some of the tests and then disappeared at the end of about twelve hours. This was finally traced to test bottles which were rinsed with alcohol, then with ether, and the caustic put in before the bottles were fully dry. Various kinds of potassium hydroxide were investigated before the cause of the color was discovered and it may be remarked that the test is not much influenced by the purity of the alkali. Obviously, however, the pure white sticks are the best to use in this test.

Acroleïn and furfural, if added in small quantities to ether, impart a color to potash similar to the aldehyde color. Paraldehyde in traces produces no color in this test unless the ether containing it is previously warmed with a drop of sulfuric acid, which suffices to liberate the aldehyde. These substances, however, are not known to occur in ethers of modern manufacture. A more likely source of trouble lies in the use of ordinary corks for, as pointed out by Baskerville,[3] ether may dissolve substances from cork which cause the potash to discolor in the absence of aldehyde.

Test for Foreign Odors

The usual practice is to evaporate slowly on a steam-bath, without rapid boiling, 30 cc. of the ether to be tested in a small beaker covered with a watch glass. When the ether has evaporated to a residue of one or two cubic centimeters, the residue is poured drop by drop on the center of a clean piece of filter paper; four inches square is a convenient size. The evaporation keeps up with the dropping and a spot about the size of a half dollar is formed. Practice enables one to judge when the ether has almost disappeared and at this instant the wet spot, which now contains the

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[13] Mallinckrodt and Alt, *J. Ind. Eng. Chem.*, **8**, 807 (1916).

substances less volatile than ether, should be placed close to the nostrils and smelled. With pure ether containing little or no odor, the damp spot at the center of the paper may be laid over the nostrils and air drawn into the nose. This test is so sensitive that an aroma different from the smell of ether itself may be detected with nearly every ether, no matter how prepared, and good judgment should be used in interpreting the results. The value of such a sensitive test lies in concentrating any traces of irritating substances present in the ether, which are masked more or less by the smell of the ether itself, and presenting them to the nostrils in such a way that their pungency or irritating effect cannot be mistaken. The appearance of the spot is very characteristic and should be carefully noted. The presence of several per cent. of alcohol may be detected by the appearance and smell of the spot. Water shows plainly by the slowness with which the spot evaporates from the paper. One drop of acetic or formic acid or one drop of oil of wine in 30 cc. of ether is easily recognized. Frequently the spot at the center of the paper on which the ether has been poured shows an oily appearance, or an oily margin about the circumference of the spot. This occurs in the case of ethers containing peroxides, due to the concentration of the latter being only slightly volatile. When such a spot is placed to the nostrils and air drawn into the nose, a very characteristic irritating odor, somewhat like pepper, is noticed which, after a few moments, becomes still more irritating to the lining of the nostrils. If a few drops of the cadmium potassium iodide reagent, as used for the peroxide test, is applied to the oily line, iodine is immediately liberated and stains the paper brown or bluish. The pure oil, on the other hand, rich in organic peroxides,[14] which we obtained by fractionation of old ether, had of itself very little odor, but if several drops are added to 30 cc. of pure ether and the odor test applied, the characteristic irritating odor of peroxidized ether appears.[15]

The odor test is of little value for detecting volatile impurities which distil with the ether vapor itself. Fortunately there are none such likely to occur in ether. A few drops of aqueous sulfurous acid in 30 cc. of ether could neither be detected by the odor test nor could it be detected by pouring the ether directly on filter paper and smelling.

In one experiment, sixty-five sealed cans of ether, averaging about one year old and ranging from about seven months to a year and a half, were found to contain fifteen cans which had pronounced bad odors. Of the fifteen bad cans, nine gave pronounced reactions for peroxides and each of the nine, when subjected to the odor test, gave the pungent, peppery

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[14] Clover (Ref. 8, p. 1112), on the other hand, found that his pure "ether peroxide" had an irritating odor.

[15] This interesting fact was noted by Dr. W. N. Stull in our Laboratory fifteen years ago and has been confirmed by later experience.

odor characteristic of peroxides. There were only two cans in the lot which gave affirmative test for peroxides which failed to give the characteristic odor, but these cans showed only a very slight reaction with the cadmium potassium iodide reagent. The close relation between the presence of peroxides and a certain kind of odor is evident.

Summary

1. Under average conditions, if ether contains less than about 0.05% of aldehyde it will probably not be detected by the official aldehyde test in U.S.P. X, whereas the test employing solid potassium hydroxide will, by employing the precautions given in this paper, detect 0.01%.

2. Peroxides and alcohol, if present in the ether, produce characteristic appearances in this test and their effects are described.

3. Shaking with metallic mercury provides a convenient means of decomposing the organic peroxides naturally occurring in old ether with liberation of acetaldehyde in accordance with the work of Clover and of Wieland and Wingler on the constitution of these peroxides.

4. The presence of more than minute traces of peroxides in ether can be detected by a characteristic odor when the ether is evaporated to small volume and smelled after pouring upon paper.

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NOTE

Reduction of Benzophenone by Magnesium Amalgam. Correction.—In a recent paper[1] we reported that magnesium amalgam did not reduce benzophenone, contrary to statements of others.[2] Because of the positive results obtained in the case of benzil[3] with magnesium amalgam, the experiments on benzophenone were repeated. We again experienced the same difficulty as before with amalgam that had been prepared as previously by heating together magnesium and mercury. However, in several instances of a number of experiments it was observed that a simple mixture of magnesium metal and mercury at room temperature effected reduction of benzophenone. We are at present at a loss to explain the differences in the results obtained.

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[1] Gomberg and Bachmann, THIS JOURNAL, **49**, 236 (1927).

[2] Schlenk and Thal, *Ber.*, **46**, 2847 (1913).

[3] Gomberg and Bachmann, THIS JOURNAL, **49**, 2584 (1927).