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CXXVIII.—*The Constitution of Acetone.*

By Millicent Taylor.

Some fifteen years ago a series of papers was published by Freer (*Amer. Chem. J.*, 1890, **12**, 356; 1891, **13**, 322; 1893, **15**, 582; *Annalen*, 1893, **278**, 116; 1894, **283**, 380), showing that sodium directly displaces hydrogen in acetone, and that the resulting "sodium acetone" yields *iso*propenyl esters with acid chlorides.

Repeated want of success in attempting to prepare *iso*propenyl esters from sodium acetone led to the further investigation of the action of sodium on acetone, and the behaviour of the resulting substances with acid chlorides.

The determination of the percentage of sodium in so-called "sodium acetone" shows that this substance consists chiefly of caustic soda mixed with a small proportion of the sodium derivatives of alcoholic reduction and condensation products of acetone.

The action of "sodium acetone" on ethyl chloro-formate yielded sodium carbonate together with small quantities of ethyl *iso*propyl carbonate and large quantities of condensation products of acetone. No indication of the formation of ethyl *iso*propenyl carbonate was obtained.

The action of "sodium acetone" on *p*-nitrobenzoyl chloride yielded *p*-nitrobenzoic acid and anhydride, sodium *p*-nitrobenzoate, and a small quantity of *iso*propyl *p*-nitrobenzoate.

The yield of these substances showed conclusively that, allowing for slight loss in the various processes carried out, the total quantity of *p*-nitrobenzoyl chloride was accounted for, and that consequently *iso*propenyl *p*-nitrobenzoate could not have been formed.

Finally, the action of Grignard's reagent on acetone itself was investigated, but only negative results were obtained, no methane being liberated.

The rapid action of sodium on an ethereal solution of acetone is probably due primarily to traces either of moisture or of caustic soda. When every precaution is taken to dry the acetone and the ether employed as solvent, sodium does not act immediately, but reaction becomes evident in a few minutes and then proceeds rapidly. Heintz (*Annalen*, 1875, **178**, 342) and later Koelichen (*Zeit. physikal. Chem.*, 1900, **33**, 129) have shown that acetone condenses at 0° and at the ordinary temperature under the influence of caustic soda, yielding diacetone-alcohol, $OH{\cdot}C(CH_3)_2{\cdot}CH_2{\cdot}CO{\cdot}CH_3$.

This ketone alcohol is readily acted on by sodium, and further loses

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water, especially in the presence of dehydrating agents, giving mesityl oxide.

It follows then that the presence of traces of caustic soda, which are most difficult to avoid, would easily account for its further formation in quantity and for the various phenomena observed.

I. *The Determination of the Percentage of Sodium in "Sodium Acetone."*

The ether used in this experiment was dried over phosphorus pentoxide, then left for a week in the dark over repeatedly renewed sodium and potassium wire, and finally boiled for some hours with these metals. The acetone was shaken repeatedly with phosphorus pentoxide and distilled through a Young's still-head. It boiled constantly at 56·2° under 760 mm. The hydrogen was purified by means of caustic soda, soda-lime, calcium chloride, sulphuric acid, and phosphorus pentoxide.

The apparatus was arranged exactly as described by Freer (*Amer. Chem. J.*, 1893, **15**, 587), except that a slight modification was introduced in order to bring about more rapid filtration.

The sodium dissolved with the formation of a white precipitate which settled rapidly, and this was followed by the gradual separation of a less dense red substance. After standing for one hour, the precipitate was washed by decantation with absolute ether, and finally some of it was drawn into a funnel tube, washed, and dried in a current of hydrogen until there was no further decrease in weight. The solid was then dissolved in water and titrated with normal sulphuric acid.

0·6275 required 10·25 c.c. *N*-sulphuric acid. Na = 37·5.
"Sodium acetone" requires Na = 28·75 per cent.

A second determination of the sodium in the precipitate, which had been left for twenty-four hours in an atmosphere of hydrogen, showed that the percentage of sodium had decreased.

0·7968 required 11·5 c.c. *N*-sulphuric acid. Na = 33.

The latter result is approximately the percentage of sodium required by "sodium acetone," but since there was no doubt that the formation of the red substance was due to some secondary change, and not to the direct action of sodium on acetone, the solid was not allowed to settle in the next experiments, but the liquid was filtered as soon as it was certain that the whole of the sodium had dissolved.

In two experiments, therefore, 0·7 gram and 0·5 gram of sodium respectively were dissolved in a larger proportion of acetone than had been used previously; in five minutes, the whole of the sodium had disappeared, and the mixture was then stirred for ten minutes, the

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precipitate collected, dried in a current of hydrogen until its weight was constant, then dissolved in water and titrated with standard sulphuric acid.

Expt. II. 0·2619 required 114·8 c.c. $N/20$ H_2SO_4. Na = 50·4.
Expt. III. 0·4806 „ 105·4 c.c. $N/10$ H_2SO_4. Na = 50·4.
NaOH requires Na = 57·5 per cent.

The ethereal solution in experiments I and III was evaporated in a current of hydrogen. It contained the red precipitate which formed after decantation or filtration, and also some liquid condensation products of acetone, so that the result is of no value as indicating the composition of the red substance.

Expt. I. 0·69 of residue required 35·6 c.c. $N/10$ H_2SO_4. Na = 11·9.

Expt. III. 1·645 of residue required 82·5 c.c. $N/10$ H_2SO_4. Na = 11·5 per cent.

This result is recorded because it has been stated (*Amer. Chem. J.*, 1893, **15**, 587; *Annalen*, 1893, **278**, 116) that this residue has a composition identical with that of the first precipitate and approximately that of "sodium acetone."

II. *The Action of Ethyl Chloro-formate on "Sodium Acetone."*

The reaction was carried out several times under slightly different conditions and using different quantities of materials, but always in accordance with the directions given by Freer (*Amer. Chem. J.*, 1891, **13**, 319; *Annalen*, 1894, **283**, 380).

In each case the result was the same. Large quantities of difficultly-volatile condensation products of acetone were obtained, together with a mixture consisting almost entirely of mesityl oxide, diethyl, ethyl *iso*propyl and di-*iso*propyl carbonates, boiling between 120° and 140°.

Details of three of these preparations are recorded here, as the results not only give no indication of the production of ethyl *iso*propenyl carbonate, but they afford a totally different and yet satisfactory explanation of the facts which have been interpreted as indicating the formation of that ester.

Preparation I.—The volatile products of the reaction, after treatment with phenylhydrazine (the substance used by Freer to remove condensation products of acetone), gave on analysis a percentage of carbon greatly in excess of that calculated for ethyl *iso*propenyl carbonate. The substances containing this high percentage of carbon can be removed by phenylhydrazine, but only on prolonged treatment

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with this reagent, and they are rapidly decomposed by dilute sulphuric acid, leaving only ethyl *iso*propyl carbonate.

Condensation products of acetone would, however, contain a higher percentage of carbon than ethyl *iso*propenyl carbonate, and, moreover, are decomposed by dilute sulphuric acid with formation of acetone; so that although the results of this preparation do not prove the absence of ethyl *iso*propenyl carbonate, they certainly indicate that such condensation products, which I have shown are difficult to remove, may be the source of the acetone stated (*Annalen*, 1894, **283**, 380) to have been obtained by saponification of the esters.

Ten grams of sodium, in separate quantities of one gram, were treated with acetone in ethereal solution, and subsequently with ethyl chloroformate, as described by Freer (*Amer. Chem. J.*, 1891, **13**, 319). The ether was evaporated and the residue fractionated under a pressure of 250 mm., when half of the liquid product passed over between 90° and 110°. After treatment with phenylhydrazine, the liquid was distilled with steam, dried, and repeatedly fractionated. The largest fraction boiled between 95° and 96° (250 mm.) and gave the following data on analysis:

0·2102 gave 0·4774 CO_2 and 0·1858 H_2O. C = 61·94; H = 9·82.
Ethyl *iso*propenyl carbonate, $C_6H_{10}O_3$, requires C = 55·38; H = 7·69.
Mesityl oxide, $C_6H_{10}O$, requires C = 73·47; H = 10·20 per cent.

It was found that the liquid boiling between 95° and 96° was capable of reacting still further with phenylhydrazine, although the reaction was extremely slow, and after being allowed to remain in contact with excess of this reagent for four days, it was again purified, and the analyses given below show that a further quantity of some condensation product of acetone had been removed.

0·2886 gave 0·2482 H_2O and 0·6358 CO_2. C = 59·46; H = 9·56 per cent.

Five grams of this liquid were then digested for about fifteen minutes on the water-bath with very dilute sulphuric acid, to decompose condensation products of acetone. As soon as the slow formation of small bubbles of gas indicated the incipient decomposition of carbonic esters, the remaining liquid was washed, dried over calcium chloride, and distilled.

It was then found to boil between 91° and 94° under 200 mm. pressure, and appeared from the analysis to be almost pure ethyl *iso*propyl carbonate.

(I) 0·2739 gave 0·5497 CO_2 and 0·2246 H_2O. C = 54·78; H = 9·11.
(II) 0·1147 ,, 0·2300 CO_2 and 0·0953 H_2O. C = 54·68; H = 9·23.
$C_6H_{12}O_3$ requires C = 54·54; H = 9·09 per cent.

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A comparison of the properties of this substance with synthetic ethyl *iso*propyl carbonate, formed by the action of ethyl chloro-formate on sodium *iso*propoxide, showed that the two were identical in every respect. The boiling points were 92° to 94° (200 mm.) and 130° to 134° (760 mm.).

0·3395 gave 0·6812 CO_2 and 0·2763 H_2O. C = 54·70; H = 9·04.

Now, had ethyl *iso*propenyl carbonate been present, it would very probably have been decomposed by the sulphuric acid, but the amount must have been small, since the digestion was stopped and the acid removed on the first indication of the liberation of carbon dioxide. The chief value of this result, however, lies in the fact that it indicates the presence, with the carbonic esters, of condensation products of acetone, which, though readily decomposed by dilute acid, are not so easily removed by phenylhydrazine.

Preparation II.—Since it was possible that digestion with dilute sulphuric acid or even prolonged treatment with phenylhydrazine might bring about the decomposition of ethyl *iso*propenyl carbonate, a much larger quantity of material was prepared and an attempt was made to isolate the latter ester by repeated fractionation. The product from 300 c.c. of acetone, 32 grams of sodium, and 140 c.c. of ethyl chloro-formate yielded 75 grams of liquid, boiling below 134°, and this, on repeated fractionation under atmospheric pressure, gave two large fractions. The first boiled at 127—127·5°, and on analysis:

0·2664 gave 0·5604 CO_2 and 0·2188 H_2O. C = 57·37; H = 9·13;

the other, which boiled at 127·5—128·2°, was also analysed:

0·3090 gave 0·6510 CO_2 and 0·2554 H_2O. C = 57·44; H = 9·18.
0·3215 „ 0·6738 CO_2 and 0·2663 H_2O. C = 57·15; H = 9·20;
whilst ethyl *iso*propenyl carbonate requires C = 55·38; H = 7·69 per cent.

The united liquids were then left in contact with phenylhydrazine for a fortnight, purified as previously described, and repeatedly distilled under atmospheric pressure with a five-section Young's still-head. Four fractions having the following characters were obtained:

Fraction I, 125—126°. 0·1570 gave 0·2940 CO_2 and 0·1309 H_2O. C = 51·07; H = 8·56.

Fraction II, 127—128°. 0·2552 gave 0·4974 CO_2 and 0·2004 H_2O. C = 53·15; H = 8·73.

Fraction III, 129—130°. 0·3138 gave 0·6112 CO_2 and 0·2491 H_2O. C = 53·12; H = 8·84.

Fraction IV, 130—132°. 0·3069 gave 0·6067 CO_2 and 0·2482 H_2O. C = 53·91; H = 8·99.

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Fraction I was evidently nearly pure diethyl carbonate (b. p. = 126°; C = 50·85; and H = 8·48 per cent.), and the others appear to consist of diethyl carbonate mixed with ethyl *iso*propyl carbonate. Freer, who found the vapour density of the fraction 129—130° to be 4·44, concluded that this was nearly pure ethyl *iso*propenyl carbonate, but the vapour density of a mixture of diethyl carbonate and ethyl *iso*propyl carbonate having the composition indicated by the above analysis would have nearly the same vapour density, namely, 4·38.

The fraction 130—132°, containing about 83 per cent. of ethyl *iso*propyl carbonate and 17 per cent. of diethyl carbonate, should yield 34 per cent. of carbon dioxide on hydrolysis: Freer actually found 33·89 per cent.

Preparation III.—The results just recorded indicate the formation of a large quantity of diethyl carbonate, and on repeating the experiment precautions were taken wholly to remove all alcohol from the ether employed as a diluent.* The acetone was obtained by fractionation of a dried specimen from the bisulphite compound and boiled at 56—56·5°, and the ethyl chloro-formate was dried over phosphorus pentoxide and boiled at 90·5° under 733 mm. pressure. It was found that the yield of liquid boiling at 120—140° was much reduced, and after treatment with phenylhydrazine was finally resolved by distillation at a pressure of 200 mm. with a three-section Young's still-head into the following portions, each weighing from 2 to 3·2 grams.

(I) B. p. 86—88°. 0·2145 gave 0·4220 CO_2 and 0·1716 H_2O. C = 53·66; H = 8·89.

(II) B. p. 88—90°. 0·1792 gave 0·3570 CO_2 and 0·1467 H_2O. C = 54·04; H = 9·02.

(III) B. p. 90—92°. 0·2319 gave 0·4571 CO_2 and 0·1860 H_2O. C = 53·74; H = 8·91.

(IV) B. p. 92—94°. 0·1868 gave 0·3778 CO_2 and 0·1532 H_2O. C = 55·16; H = 9·11.

(V) B. p. 94—96°. 0·1916 gave 0·3858 CO_2 and 0·1604 H_2O. C = 54·92; H = 9·30.

Assuming that the residue in the still-head had the same composition as the last fraction, the mean percentage of carbon and hydrogen in the fractionated liquid was C = 54·37; H = 9·08 per cent.

In no case, it will be seen, does the amount of hydrogen approach the number calculated for ethyl *iso*propenyl carbonate, and the analyses

* This is a matter of considerable difficulty unless phosphorus pentoxide as well as sodium is used for the purpose; there can be no doubt that Freer's results also were due to the presence of alcohol in the ether employed by him (*Amer. Chem. J.*, 1893, **15**, 590).

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indicate that the liquid consisted of ethyl *iso*propyl carbonate, which appears to decompose slightly on distillation even under reduced pressure into diethyl and di*iso*propyl carbonates.

Saponification of the Esters.

Fifteen grams of the various fractions boiling under atmospheric pressure from 127° to 133° were saponified on a water-bath with dilute hydrochloric acid, great care being taken that no volatile products escaped. One gram of unsaponifiable oil was obtained, and a liquid which, after drying and distilling, boiled between 78° and 82° and weighed between 9 and 10 grams. Since the theoretical yield of alcohols from 14 grams of mixed esters is about 11 grams, it is evident that acetone has neither been lost nor destroyed during these processes. On fractionating the liquid, no traces of the more volatile substance could be obtained, although every precaution was taken. The results of the fractionation were as follows:

(I) 77·5—79·5°, 4·6 grams; (II) 79·5—80·0°, 1·6 grams; (III) above 80°, 2·5 grams.

An analysis of the first fraction showed that it was pure ethyl alcohol.

0·3270 gave 0·6263 CO_2 and 0·3838 H_2O. C = 52·25; H = 13·04.
C_2H_6O requires C = 52·17; H = 13·04 per cent.

Evidently then the ethyl and *iso*propyl alcohols obtained are quite free from acetone.

The products of higher boiling point were distilled under a pressure of 30 mm., and the distillate which passed over between 130° and 170° partially crystallised on standing. The semi-solid mass was drained on a porous tile and recrystallised from ether, when a crystalline substance, melting at 177°, was obtained, which volatilised without decomposition under atmospheric pressure. On boiling with soda or baryta, the substance decomposed, yielding carbon dioxide, but the amount available was insufficient for further examination. It crystallised with unchanged melting point after dissolving in ether and treatment with phenylhydrazine.

The molecular weight was determined by the ebullioscopic method, using benzene as solvent.

(I) 0·1975 gram in 12·83 grams of benzene raised the boiling point 0·250°; molecular weight, 164·4.

(II) 0·3023 gram in 12·83 grams of benzene raised the boiling point 0·354°; molecular weight, 177·7.

The vapour density was determined by V. Meyer's method, using a hot-air jacket.

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(I) 0·1936 gave 22·5 c.c. at 16° and 757 mm.; molecular weight = 208.

(II) 0·1983 gave 23·5 c.c. at 16·5° and 757 mm.; molecular weight = 204.

On analysis:

(I) 0·2087 gave 0·4567 CO_2 and 0·1595 H_2O. C = 59·69; H = 8·55.
(II) 0·1657 „ 0·3603 CO_2 „ 0·1278 H_2O. C = 59·86; H = 8·57.
$C_{10}H_{18}O_4$ requires C = 59·41; H = 8·91 per cent., and molecular weight = 202.

It is probable that this substance is *diacetone* iso*propyl carbonate*,

$$(CH_3)_2C(\cdot O\cdot CO_2\cdot C_3H_7)\cdot CH_2\cdot CO\cdot CH_3,$$

since diacetone alcohol, $(CH_3)_2{:}C\cdot(OH)\cdot CH_2\cdot CO\cdot CH_3$, is produced by the action of alkalis on acetone (Koelichen, *Zeit. physikal. Chem.*, 1900, **33**, 129).

III. *The Action of* p-*Nitrobenzoyl Chloride on "Sodium Acetone."*

The difficulty of investigating the action of ethyl chloroformate on "sodium acetone" arose from the fact that the boiling points of the esters formed lie very near the boiling point of mesityl oxide. Their isolation is consequently impossible unless some reagent such as phenylhydrazine is used to remove the mesityl oxide, and it is conceivable that long standing with this substance might decompose ethyl *iso*propenyl carbonate. This difficulty does not arise if the acid chloride employed yields solid esters.

p-Nitrobenzoyl chloride was found to be very suitable, not only on account of its crystalline esters, but because the anhydride is almost insoluble in water and ether, and can be easily separated from the other products of the reaction, consequently allowing a determination of the yield of each product. It was found that the whole of the acid chloride employed was converted into acid anhydride, acid (or sodium salt), and *iso*propyl ester, leaving no possibility of the formation of other compounds. The action of the so-called "sodium acetone" on *p*-nitrobenzoyl chloride therefore consists entirely in the action of caustic soda mixed with some sodium *iso*propoxide on the latter substance. The reaction was carried out under the same conditions as those described by Freer (*Amer. Chem. J.*, 1893, **15**, 595) in the case of benzoyl chloride, and the ether, hydrogen, and acetone were purified as previously described. After recrystallising from chloroform, the *p*-nitrobenzoyl chloride, which melted sharply at 73°, was dissolved in four or five times its weight of ether and then added to the "sodium acetone."

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Preparation I.—Altogether 20 grams of sodium were dissolved in 200 c.c. of acetone, and 153 grams of *p*-nitrobenzoyl chloride (the calculated quantity is 161 grams) were subsequently added. The "sodium acetone" was cooled by ice-water during the addition of the acid chloride. After long standing in an atmosphere of hydrogen, the products of the reaction consisted of a brown, insoluble substance and a dark ethereal solution with acid properties. The former was a mixture of sodium chloride, sodium nitrobenzoate, and the anhydride of nitrobenzoic acid. The anhydride melted between 175° and 178°, and, after reprecipitation from benzene by light petroleum, consisted of an ochreous, amorphous substance melting from 175° to 179°.

0·4763 gave 37·6 c.c. of moist nitrogen at 15·5° and 736 mm. N = 8·94.
p-Nitrobenzoic anhydride, $C_{14}H_8O_7N_2$, requires N = 8·86 per cent.

The ethereal solution was freed from nitrobenzoic acid and a little anhydride by repeatedly shaking, first with sodium hydrogen carbonate solution until the latter gave only a faint cloudiness on acidifying, and then with sodium carbonate. Caustic soda was not employed at this stage, as it was conceivable that any unstable ester present might be decomposed by the alkali. The ether was then evaporated from the dried solution, and, after standing some time, brown crystals separated from the oily residue. These were drained at the pump, and about 8 grams of crystals, melting from 95° to 103°, were obtained eventually. The ethereal solution of the crystals was shaken up with 1 per cent. caustic soda solution, which extracted less than 0·6 gram of acid, so that evidently no easily decomposable ester was present. On recrystallisation from ether, the crystals melted between 107° and 108°.

0·1616 gave 0·3479 CO_2 and 0·0820 H_2O. C = 58·71 ; H = 5·64.

After sublimation, the crystals melted at 108°.

0·1841 gave 0·3897 CO_2 and 0·0902 H_2O. C = 57·72 ; H = 5·44.
*iso*Propyl *p*-nitrobenzoate, $C_{10}H_{11}O_4N$, requires C = 57·42 ; H = 5·26.
*iso*Propenyl *p*-nitrobenzoate, $C_{10}H_9O_4N$, ,, C = 57·97 ; H = 4·32 per cent.

iso*Propyl* p-*nitrobenzoate* was then synthesised by the action of *p*-nitrobenzoyl chloride on potassium *iso*propoxide in order to compare its properties with those of the above substance. After recrystallisation from ether it melted at from 95° to 107°; after sublimation, at from 107° to 108°; and on resublimation, at 108°.

0·2166 gave 12·7 c.c. of moist nitrogen at 12·5° and 762 mm. N = 6·97.
*iso*Propyl *p*-nitrobenzoate, $C_{10}H_{11}O_4N$, requires N = 6·70 per cent.

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This places beyond doubt the identity of *iso*propyl *p*-nitrobenzoate with the only ester obtained by the action of *p*-nitrobenzoyl chloride on "sodium acetone."

Preparation II.—In a second experiment, 10·4 grams of sodium dissolved in excess of acetone were allowed to react with 83·5 grams of *p*-nitrobenzoyl chloride; these proportions differ from those taken in the first experiment only in the fact that in this case the calculated quantity of chloride was used. This was found to make the separation of the various products in a state of comparative purity much easier. Scarcely any sodium *p*-nitrobenzoate was found in the products soluble in water, and the proportion of acid was smaller, and of the anhydride much larger, than in the last case. After the reaction was complete, 59 grams of chloride were recovered as anhydride, 20 grams as acid, and 2 or 3 grams as ester (m. p. 108° after purification), making up altogether 81 to 82 of the total 83·5 grams used. There is no doubt that the remaining 2 or 3 grams can be accounted for by the solubility of the acid in water, some being lost in the aqueous washings, in the sodium hydrogen carbonate, and other solutions after acidifying, and also by the fact that it was impossible to separate the whole of the ester from the condensation products of acetone.

It can therefore be definitely stated that the action of so-called "sodium acetone" on *p*-nitrobenzoyl chloride is no other than that of caustic soda and sodium *iso*propoxide on the latter substance.

With the object of obtaining definite knowledge of the properties of *iso*propenyl esters, and so ensuring their recognition, several attempts were made under varying conditions to prepare *iso*propenyl *p*-nitrobenzoate by the action of the silver salt on β-bromopropylene, $CH_3 \cdot CBr{:}CH_2$.

In every case a negative result was obtained; a very small quantity of *p*-nitrobenzoic acid was isolated, but nearly the whole of the silver salt remained undecomposed, and no ester could be detected.

This result was not unexpected, as other halogen derivatives of allylene and propylene have been observed by Reboul (*Ann. Chim. Phys.*, 1878, **14**, 435) and Oppenheim (*Bull. Soc. chim.*, 1865, [ii], **4**, 434) to show similar stability towards silver and potassium salts.

In conclusion, I wish to express my thanks to Dr. Francis, of University College, Bristol, for his advice and suggestions throughout the work.

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