

CCV.—*The Reactions of a Mixture of Ethyl Ether,
Acetyl Bromide, and Naphthol.*

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ALTHOUGH the reaction between acid anhydrides and hydroxy-compounds has been studied in some detail, comparatively little seems to have been attempted in connexion with the corresponding

reaction between acyl halides and hydroxy-compounds. Cohen (J., 1906, **89**, 1482) observed the temperatures at which reaction set in between menthyl alcohol and various substituted benzoyl chlorides, and Bruner and Tolloczko (*Chem. Centr.*, 1900, II, 257) determined velocity coefficients for the action of benzoyl chloride on various alcohols, using a large excess of the alcohol.

Preliminary experiments with equivalent proportions of acetyl chloride and various alcohols in ethereal solution showed that the reaction could be followed with ease, that it was bimolecular, and that the values obtained for the velocity coefficients agreed with the known order of reactivity of the alcohols used.

The method employed was to mix equivalent amounts of acetyl chloride and the alcohol in ethereal solution in a thermostat at 25°. Portions were withdrawn at intervals, quenched with excess of water, and titrated with alkali (compare Rule and Paterson, J., 1924, **125**, 2155). According to the equation $R\cdot OH + CH_3\cdot COCl = RO\cdot CO\cdot CH_3 + HCl$, the initial titration should drop to half value at the end of the reaction, since the hydrogen chloride remains unused, and this in fact was found to be approximately the case.

It was then decided to apply the same procedure to the naphthols and their derivatives with a view to investigate the various factors which might influence the reactivity of their hydroxyl groups.

Acetyl chloride was found to react too slowly and acetyl bromide was therefore used, repeated experiments having shown that acetyl bromide under the conditions employed, and in the absence of naphthol, gives no detectable reaction with ether over periods longer than those with which we were concerned.

The results were unexpected. It was found impossible to obtain constancy in the values of k except during a period in the early part of the reaction, and here, except in the more dilute solutions, the reaction was unimolecular. Further, instead of stopping at half the initial titration, the amount of acid present dropped considerably below this value and the solid residue left on evaporation of the solvent proved to be almost entirely unchanged naphthol, together with a little naphthyl acetate. The results were practically the same with either 1-naphthol or 2-naphthol.

Distillation of the liquid and extraction of the solid residue showed that at the end of the reaction there were present ethyl bromide, ethyl acetate, acetic acid, naphthol, and a little naphthyl acetate. No hydrogen bromide was detected if the mixture had been kept for about a fortnight, but at the end of shorter periods some was always present. Attempts to estimate the ethyl bromide and ethyl acetate in the distillate were not altogether satisfactory. The

results were, however, sufficiently good to show that all, or practically all, the bromine of the acetyl bromide appears as ethyl bromide and that the yield of ethyl acetate is considerably lower. This negated the idea that the products were due simply to the action of acetyl bromide on ether.

The course of the reaction was then followed by making up mixtures containing one mole each of ether, acetyl bromide, and naphthol, quenching such mixtures with metallic calcium at different intervals of time, and estimating, by a method detailed later, the ethyl bromide, naphthol, and naphthyl acetate present. It proved extremely difficult to get consistent results for ethyl acetate and the figures recorded for this substance can only be regarded as approximate. Since after periods of a fortnight or longer no hydrogen bromide or acetyl bromide could be detected, any acidity after such periods is due entirely to acetic acid.

Starting with one mole each of the three reactants, the following table indicates the final distribution of the acetyl radical and bromine actually recovered :

	1-Naphthol.	2-Naphthol.
As naphthyl acetate	0% *	15%
As ethyl acetate	33	45
As ethyl bromide	98	100
As acetic acid	53	26
Total acetyl group recovered	86	86
Total bromine recovered	98	100

* Too small an amount to estimate.

In the case of 1-naphthol, the small amount of naphthyl acetate found at the end, and the correspondingly large amount of acetic acid, is no doubt due to the greater ease of hydrolysis of 1-naphthyl acetate as compared with 2-naphthyl acetate. For the same reason there is some loss of 1-naphthyl acetate in the estimation by the calcium method owing to hydrolysis by the calcium hydroxide formed. This loss would be especially appreciable when only small amounts are present. That some 1-naphthyl acetate is in fact present was proved beyond question by the melting point of the residue and by its extraction with alkali. In no single experiment throughout this work has a naphthol residue been found entirely free from naphthyl acetate.

While, however, the amounts of naphthyl acetate found at the end are small, at intermediate stages of the reaction considerable quantities are present. Naphthyl acetate is, therefore, first formed and then decomposed during the course of the reaction.

As a result of all the observations made, we consider that the reactions taking place in mixtures of naphthol, acetyl bromide, and ether may be represented by the following equations :

1. $C_{10}H_7 \cdot OH + CH_3 \cdot COBr = C_{10}H_7 \cdot OH, CH_3 \cdot COBr.$
2. $C_{10}H_7 \cdot OH, CH_3 \cdot COBr = C_{10}H_7 \cdot O \cdot CO \cdot CH_3 + HBr.$
3. $2HBr + (C_2H_5)_2O = 2C_2H_5Br + H_2O.$
4. $C_{10}H_7 \cdot O \cdot CO \cdot CH_3 + H_2O = C_{10}H_7 \cdot OH + CH_3 \cdot CO_2H.$
5. $2CH_3 \cdot CO_2H + (C_2H_5)_2O = 2CH_3 \cdot CO \cdot O \cdot C_2H_5 + H_2O.$

Although there must be overlapping, it is considered that these five reactions are in the main consecutive and that the order in which they are written also represents the order of their velocities, No. 1 being the most rapid.

As will be shown, the changes taking place are such that no equilibrium is ever reached. The expression "end of the reaction," which for convenience has to be used frequently, is therefore employed to indicate a point after which the reactions become immeasurably slow. It will be most convenient to discuss the equations in turn.

The Formation of Naphthyl Acetate.—The amount of naphthyl acetate present reaches a maximum early in the reaction and thereafter decreases rapidly. In the mixtures containing one mole each of naphthol, acetyl bromide, and ether, the maximum is attained with 1-naphthol after 4—5 hours and the amount of naphthyl acetate present is about 60% of the theoretical yield. With 2-naphthol the maximum is reached after about 6 hours and the amount of acetate present is slightly lower. The accumulation of this large amount of naphthyl acetate clearly shows that the formation of the acetate is more rapid than its decomposition.

The suggestion of the formation of a double compound as the first stage of such a reaction is not novel (Michael and Murphy, *Annalen*, 1908, **363**, 94). It is inferred here on the ground that in the mixtures containing more ether, for which velocity coefficients were determined, the results agree with a unimolecular reaction except at the lowest concentrations used, where the reaction becomes bimolecular. It would appear, therefore, that in dilute solutions the formation of the double compound becomes the slower reaction and so determines the measured order of the reaction. Naturally, in ether the values of k only show reasonable constancy over a period of some hours early in the reaction before the secondary changes have become important. In benzene, however, where the solvent is not involved, the same phenomenon is observed of a change, on dilution, from a unimolecular reaction to a bimolecular. In benzene the unimolecular stage persists to a greater dilution than in ether.

The Formation of Ethyl Bromide.—At first sight the production of ethyl bromide and ethyl acetate from acetyl bromide and ether would appear to indicate a simple reaction between these two substances. Descudé (*Compt. rend.*, 1901, **132**, 1129) has obtained

such a result quantitatively in the presence of zinc chloride. In the present case, however, the ethyl bromide and ethyl acetate are produced quite independently of each other. If they were produced directly by the action of acetyl bromide on ether, they would necessarily be formed at precisely the same rate and to the same extent. In fact, the whole of the bromine of the acetyl bromide, as well as the small amount of hydrogen bromide present in the acetyl bromide used, is converted into ethyl bromide. This was shown by direct and by indirect estimations of ethyl bromide and also by the fact that not a trace of hydrogen bromide or acetyl bromide remains at the end of the reaction. On the other hand, the yields of ethyl acetate fall far short of the theoretical and a considerable percentage of the acetyl radical is found in the form of acetic acid.

The ethyl bromide must, then, be formed by the action of hydrogen bromide on ether. Ether is of course known to react with hydrogen halides in this way (*e.g.*, Cottrell and Rogers, *J. Amer. Chem. Soc.*, 1899, **21**, 64), but the reaction here is more rapid than would be expected and it is suggested that the reaction is catalysed by the naphthyl acetate. There would be a tendency for this in that the water produced by the reaction is used up by the naphthyl acetate (see below).

The Formation of Acetic Acid.—Since at the end of the reaction the mixtures are entirely free from hydrogen bromide and acetyl bromide, the whole of the acidity at this stage is due to acetic acid. The latter was actually isolated and formally identified by boiling point. The acetyl bromide used contained a little acetic acid, but the amounts found at the end very greatly exceeded this original small amount.

Naphthyl acetate is hydrolysed by water and this hydrolysis is more rapid in the presence of hydrogen bromide. The products of hydrolysis are, of course, naphthol and acetic acid. The necessary water arises from the reaction between hydrogen bromide and ether. This, then, accounts for the reversion of naphthyl acetate to naphthol and for the production of the acetic acid, but as the reaction is much slower than the formation of the acetate, it permits the accumulation of acetate in the early stages of the process.

It is to be noted, however, that the amount of water formed by the reaction between ether and a given quantity of hydrogen bromide is only sufficient to hydrolyse half the naphthyl acetate produced at the same time as this quantity of hydrogen bromide. The point is discussed further in the next section. The hydrolysis will become slower as the hydrogen bromide is removed from the system and for this reason, as well as on account of a deficiency of water, the

hydrolysis of naphthyl acetate will become very slow towards the end. In actual fact, an appreciable quantity remains even after several months, and, as will be shown, some must always remain unchanged. Since 1-naphthyl acetate is much easier to hydrolyse than the 2-naphthyl compound, there is less acetate left at the end in the case of 1-naphthol than with 2-naphthol.

This explanation of the reversion of naphthyl acetate to naphthol is further confirmed by the fact that naphthyl acetate and hydrogen bromide in benzene solution do not react, whereas on addition of a little ether to the mixture naphthol is obtained.

The Formation of Ethyl Acetate.—It has been previously shown that acetic acid will react with ether at the ordinary temperature in the presence of dry hydrogen bromide to form ethyl acetate (Fenton and Gostling, J., 1898, **73**, 555). This reaction is considered to account for the production of the ethyl acetate in the present instance. Since the production of the necessary acetic acid depends on the disappearance of the hydrogen bromide in forming the required water, there must come a point where acetic acid is present but no hydrogen bromide to catalyse its reaction with ether. One would therefore expect to find a considerable quantity of free acetic acid at the end, especially in the mixtures containing a small amount of ether, where the active mass of the ether late in the reaction is small.

As a consequence, and also because there is always some unchanged naphthyl acetate, the amount of ethyl acetate produced can never be equal to that of ethyl bromide.

The water formed during the reaction between acetic acid and ether goes to hydrolyse more naphthyl acetate, but throughout the reactions water is produced in ever-diminishing quantity and can never, as was pointed out before, be quite sufficient to hydrolyse all the naphthyl acetate. The point is made clearer by writing all the equations with such quantities as to give one molecule of water at the end :

1. $4C_{10}H_7 \cdot OH + 4CH_3 \cdot COBr = 4C_{10}H_7 \cdot OH, CH_3 \cdot COBr.$
2. $4C_{10}H_7 \cdot OH, CH_3 \cdot COBr = 4C_{10}H_7 \cdot O \cdot CO \cdot CH_3 + 4HBr.$
3. $4HBr + 2(C_2H_5)_2O = 4C_2H_5Br + 2H_2O.$
4. $2C_{10}H_7 \cdot O \cdot CO \cdot CH_3 + 2H_2O = 2C_{10}H_7 \cdot OH + 2CH_3 \cdot CO_2H.$
5. $2CH_3 \cdot CO_2H + (C_2H_5)_2O = 2CH_3 \cdot CO \cdot O \cdot C_2H_5 + H_2O.$

The acetyl bromide used throughout these experiments contained, as was pointed out, a little hydrogen bromide and acetic acid, but since both these substances are formed during the reactions, there is no reason to suppose that the results would have been in any way different if the acetyl bromide had been of the strictest purity.

E X P E R I M E N T A L.

All the experiments involving ether were carried out in thick glass bottles fitted with heavy stoppers accurately ground in and slightly smeared with vaselin. These were immersed up to the neck in a thermostat maintained at 25°. The temperature did not vary by more than 0.1° throughout any series of experiments.

For the reactions in benzene solution, to avoid loss of hydrogen bromide, it was necessary to use a special reaction vessel consisting of a stoppered wash-bottle whose outlet tubes were fitted with glass taps. By connecting a pipette by means of rubber tubing to one of the outlet tubes it was possible to withdraw liquid without loss of hydrogen bromide.

The same burettes and pipettes were used throughout, so that any errors in them are constant in all experiments.

A.R. Ether was used, dried by standing over successive quantities of freshly cut sodium, and distilled. The fraction distilling between 34.5° and 35.5° was collected.

A.R. 1- and 2-Naphthols were used after drying over calcium chloride in a desiccator for several days. Some specimens were specially purified, but no difference could be observed in the results obtained. One point of interest, however, arose during these experiments. A specimen of purified naphthol was being dried in a vacuum heater at 120° over phosphoric oxide. By accident, the temperature rose to 122° and the naphthol just melted. Thereafter, in spite of being finely powdered, it was practically insoluble in dried ether or acetone, although it dissolved immediately on addition of a drop of water. Of other specimens, which did not melt, drying over phosphoric oxide did not affect the solubility.

A.R. Acetyl bromide was used without further purification. The mean of four concordant estimations of different specimens showed it to have the following average composition: acetyl bromide 94.22, hydrogen bromide 4.16, acetic acid 1.63%.

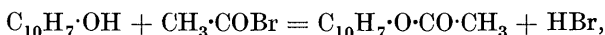
The benzene used was stirred with successive quantities of concentrated sulphuric acid until the latter was no longer discoloured, washed with water, dried over phosphoric oxide, and distilled. The fraction boiling between 80° and 81° was used.

The method of carrying out a velocity-coefficient determination was as follows: A weight of naphthol equivalent to the acetyl bromide to be used was dissolved in 25 c.c. of ether, and the acetyl bromide in sufficient ether to bring the total volume of the reaction mixture up to 50 c.c. These two solutions, in stoppered bottles, were allowed to attain 25° and then mixed in the reaction vessel. The volumes of acetyl bromide used were based on the relation 7.04 g. = 4.3 c.c. The densities of all batches of acetyl bromide

were determined, but the minute variations in density were never sufficient to warrant a departure from this value.

2 C.c. of the reaction mixture were withdrawn at intervals, run into about 30 c.c. of water, and titrated with *N*/5-potassium hydroxide solution, naphtholphthalein being used as indicator.

Calculations of the velocity coefficients are based upon the following considerations: If there were no secondary reactions and the total change could be represented by the equation



then, upon quenching a given amount of the mixture with water at any point in the reaction, there will always be present a constant quantity of hydrogen bromide and a quantity of acetic acid decreasing with the progress of the reaction. By subtracting from the titre an amount of alkali equivalent to the constant hydrogen bromide, a value is obtained in c.c. of alkali corresponding to the amount of unchanged acetyl bromide present at any given moment.

There is a period of initial disturbance and, since there are in fact secondary reactions, one could only expect reasonable constancy in the values of *k* over a comparatively short period early in the reaction before the secondary changes have set in to an important extent. Many determinations were made. The tables recorded are those showing the lowest concentrations agreeing with a unimolecular reaction and the highest showing a bimolecular reaction. All the changes, including the initial disturbance, are of course slower in the more dilute solutions.

1-Naphthol in Ethereal Solution.

8.24 G. of 1-naphthol and 7.04 g. of acetyl bromide in 50 c.c. of solution. 6.0754 G. of 1-naphthol and 5.192 g. of acetyl bromide in 50 c.c. of solution.

<i>t</i> (mins.).	<i>k</i> ₁ × 10 ³ .	<i>t</i> (mins.).	<i>k</i> ₁ × 10 ³ .	<i>t</i> (mins.).	<i>k</i> ₂ × 10 ⁵ .	<i>t</i> (mins.).	<i>k</i> ₂ × 10 ⁵ .
8.25	1.4	138.25	1.2	43.25	8.9	317	6.5
49.75	1.2	158.25	1.3	74.92	6.5	370.25	6.6
86.0	1.2	170.25	1.2	238.75	5.6	386.75	6.6
103.33	1.2	179.0	1.3	271.75	6.7		
115.5	1.2						

2-Naphthol in Ethereal Solution.

8.24 G. of 2-naphthol and 7.04 g. of acetyl bromide in 50 c.c. of solution. 6.0754 G. of 2-naphthol and 5.192 g. of acetyl bromide in 50 c.c. of solution.

<i>t</i> (mins.).	<i>k</i> ₁ × 10 ³ .	<i>t</i> (mins.).	<i>k</i> ₁ × 10 ³ .	<i>t</i> (mins.).	<i>k</i> ₂ × 10 ⁴ .	<i>t</i> (mins.).	<i>k</i> ₂ × 10 ⁴ .
12.75	3.2	87.75	3.1	60.25	2.9	235.75	2.6
20.25	3.1	105.0	3.1	88.25	2.5	248.5	2.6
30.0	3.2	124.75	3.1	169.0	2.6	266.0	2.6
40.5	3.2	138.25	3.2	187.25	2.6	278.42	2.6
57.75	3.1	160.75	3.3	215.5	2.5	301.0	2.5
69.75	3.1						

1-Naphthol in Benzene Solution.

5.0 G. of 1-naphthol and 4.272 g. of acetyl bromide in 50 c.c. of solution.				3.0 G. of 1-naphthol and 2.564 g. of acetyl bromide in 50 c.c. of solution.			
t	$k_1 \times 10^2$	t	$k_1 \times 10^2$	t	$k_2 \times 10^3$	t	$k_2 \times 10^3$
(mins.)		(mins.)		(mins.)		(mins.)	
2.83	3.2	21.75	2.7	9.25	5.4	32.33	5.9
6.42	2.6	37.33	2.6	12.17	5.8	56.75	5.7
9.25	2.8	40.58	2.5	15.67	5.5	66.58	5.7
13.17	2.6	43.58	2.6	19.58	5.2	71.83	5.7
18.5	2.7			23.0	5.2	179.0	5.6
				28.0	5.8		

In the titrations of the benzene solutions the end-point was not very sharp.

Estimations.—Distillation. Numerous attempts were made to estimate the substances present at the end of the reaction by fractional distillation and estimation of the various fractions, but the results were unsatisfactory. They merely showed that there was a high yield of ethyl bromide, a much lower yield of ethyl acetate, and, qualitatively, the presence of acetic acid and absence of hydrogen bromide and acetyl bromide.

Extraction. A mixture containing 14.125 g. of 2-naphthol, 12.12 g. of acetyl bromide, and 42.6 c.c. of ether was left in a stoppered bottle in the thermostat for 12 days. 10 C.c. of this mixture were placed in a separating funnel with excess of alkali to neutralise any free acid, and 100 c.c. of carefully purified chloroform. After shaking, the chloroform layer was removed, the extraction twice repeated, and the collected chloroform extracts placed in a flask containing excess of silver oxide in silver nitrate solution. The flask was kept in the dark until precipitation was complete. The bromine in the aqueous layer was also estimated, and represents the free hydrogen bromide. The bromine recovered was equal to 100.7% of the theoretical amount calculated on the acetyl bromide used, and the results showed that with the above mixture, in 12 days, 93.6% of the total bromine is converted into ethyl bromide.

This direct estimation of ethyl bromide is interesting as confirming the indirect estimations made later.

Estimations by the use of metallic calcium. Apart from estimating the end products, it was also desired to follow the course of the reaction and this was much more difficult because at an intermediate point the mixture of substances present is much more complex than at the end. Any process used had to be capable of being carried through in a reasonably short time so that a large number of determinations could be made.

Many methods were considered and tried, but there were fatal objections to all except to the process finally adopted, and even this left something to be desired in point of accuracy.

By estimating mixtures of known composition we found that the process of quenching the reaction by means of metallic calcium permitted the (indirect) estimation of ethyl bromide at any stage of the reaction with great accuracy and of naphthyl acetate with only a small percentage error. The estimation of ethyl acetate was not so satisfactory. The results were somewhat irregular, and only approximate figures could be obtained. These results are therefore not recorded except at the end, where there are less complications, and the figures, in consequence, are probably more accurate.

The method was as follows: Mixtures of 2.06 g. of naphthol, 1.76 g. of acetyl bromide, and 1 c.c. of ether (equimolecular proportions) were placed in wide-necked 1 oz. stoppered bottles. The stoppers were secured with wire, and the bottles placed in a thermostat at 25°. After a definite interval of time 1 c.c. of water was added to the contents of the bottle, which was then shaken and attached immediately to a reflux condenser. A few c.c. of ether were then added to dissolve the solid which was frequently present, and metallic calcium added cautiously through the condenser. The reaction which ensued was at first vigorous but was not actually complete for nearly an hour. When there was no further action on addition of fresh calcium, a few c.c. of ether were added, the mixture was stirred, and the ethereal solution filtered into a flask of 33 c.c. capacity adapted to prevent loss by bumping during the subsequent evaporation under reduced pressure. The solid was washed and stirred with further quantities of ether until the required volume of filtrate (33 c.c.) was attained.

The ethereal solution contained the naphthol, naphthyl acetate, ethyl bromide, and ethyl acetate, while the solid residue consisted of calcium bromide, acetate, and hydroxide.

Estimation of the bromide in this residue gave the bromine present in the reaction mixture in the form of acetyl bromide or hydrogen bromide at the time of quenching. The difference between this amount and the bromine of the acetyl bromide used gave the ethyl bromide.

The greater part of the ethereal solution was used for the estimation of naphthyl acetate. The volatile substances were removed by evaporation under reduced pressure. Two successive quantities of about 10 c.c. of ether were added and the evaporation was twice repeated to secure the entire removal of ethyl acetate. The remaining mixture of naphthol and naphthyl acetate was then hydrolysed with a known excess of alkali, and the naphthyl acetate thereby estimated.

Since the estimation of ethyl acetate was not satisfactory, its details need not be given. In principle it consisted in hydrolysing

a portion of the ethereal solution before removal of the volatile substances. This, after correction for the ethyl bromide hydrolysed, gave the ethyl acetate + naphthyl acetate, and therefore, by difference, the ethyl acetate.

Since the quenching is not instantaneous, it was difficult to get accurate figures for the first two or three hours.

The values obtained for 1-naphthyl acetate, especially towards the end, are probably slightly low owing to some hydrolysis by calcium hydroxide.

2.06 G. of 1-naphthol, 1.76 g. of acetyl bromide, and 1.059 g. of ether.			2.06 G. of 2-naphthol, 1.76 g. of acetyl bromide, and 1.059 g. of ether.		
Time (hrs.).	Naphthyl acetate (g.).	Ethyl bromide (g.).	Time (hrs.).	Naphthyl acetate (g.).	Ethyl bromide (g.).
4	1.600	0.549	1	0.933	0.132
5	1.600	0.618	3	1.124	0.365
6	1.411	0.653	4	1.328	0.541
8	1.251	0.773	5	—	0.625
11	0.975	0.937	6	1.446	0.702
15	0.769	1.092	8	1.200	0.836
19	0.598	1.155	12½	1.093	1.000
23	0.405	1.223	15¼	0.927	1.048
30	0.355	1.227	19	0.903	1.192
48	—	1.353	30	0.681	1.309
72	0.056	1.461	48	0.651	1.427
5 days	—	1.528	72	0.532	1.490
8 „	—	1.527	5 days	0.416	1.532
11 „	—	1.536	10 „	0.466	1.545
Ethyl acetate at 11 days = 0.45 g.			14 „	0.434	1.557
			Ethyl acetate at 14 days = 0.6 g.		

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