248. *The Effect of Alcohols on the Partial Vapour Pressure of Acetone.*

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Acetals are readily produced by the direct action of alcohols on aldehydes, but not on acetone, and the acetals from ketones have to be obtained indirectly. Vapour-pressure measurements on mixtures of acetone with the high-boiling *n*-heptyl, benzyl, and *m*-nitrobenzyl alcohols reveal both a decrease in vapour pressure with time in presence of aqueous hydrogen chloride, and a considerable decrease in vapour pressure when other known catalysts for the alcohol–aldehyde reaction are used. Errera and Seck (*Trans. Faraday Soc.*, 1938, **34**, 728) produced evidence from infra-red spectra for the formation of complexes between alcohols and acetone, but although these complexes might be the result of dipole interaction, the vapour-pressure evidence is in favour of the view that they are acetals.

Fischer and Giebe prepared acetals by the direct action of alcohols on aldehydes (*Ber.*, 1898, **31**, 545), but this reaction fails with ketones; according to Haworth and Lapworth (J., 1922, **121**, 76), this is because the expected acetals are too readily hydrolysed. The failure to prepare acetals from acetone by this method is not evidence for the non-occurrence of the reaction. Such a reaction should result in a lowering of the partial vapour pressure of acetone over the mixture, but as it cannot be assumed that such mixtures obey Raoult's law, we do not know what the vapour pressure in the absence of the reaction ought to be. The lowering of the vapour pressure may be attributed to dipole interaction as has been suggested by Martin and Brown (*Trans. Faraday Soc.*, 1938, **34**, 742) for mixtures of methyl, ethyl, and *n*-propyl alcohols with water. Errera and Seck (*loc. cit.*) show from infra-red spectra that alcohols do form complexes with acetone which change but little with temperature and still exist in solution in ternary mixtures. It is probable that complexes resulting from dipole interaction would partly dissociate with rise of temperature, and their concentration would certainly be affected by dilution. It may well be that Errera and Seck's complexes are acetals.

This theory as to the nature of the complexes is supported by the author's vapour-pressure measurements upon mixtures of benzyl, *m*-nitrobenzyl, and *n*-heptyl alcohols with acetone. The formation of complexes should lead to negative deviations from Raoult's law, or at least a diminution in the positive deviation, but this result could also be attributed to dipole interaction. On the other hand, a decrease of vapour pressure with time could only result from compound formation and not from mere physical association. The deviations from Raoult's law in the case of benzyl alcohol and *m*-nitrobenzyl alcohol solutions are negative, as expected, and those from *n*-heptyl alcohol solutions positive but less so than might have been expected by comparison with other acetone mixtures. A decrease of vapour pressure with time has been observed in all three cases, and most markedly in the last. Further, the partial vapour pressure of the acetone has been found to be diminished by catalysts for Fischer's acetal synthesis, but not so much by aqueous hydrogen chloride, which would favour hydrolysis.

The vapour pressures were measured by the author's method (J., 1933, 204), by the Bremer–Frowein tensimeter, the isoteniscope, and by the Ramsay–Young method to determine the total vapour pressure in mixtures containing hydrogen chloride and hence the correction π for vapour other than acetone in the formula $p = 760(P - h - \pi)v/P(V + v)$

used for calculating the partial vapour pressure of acetone. In anhydrous mixtures such measurements supplemented those made by the chemical method. The static are less accurate than the dynamic methods for dilute solutions of a highly volatile substance such as acetone because they lead to high results unless the mixtures are rigorously degassed, and this involves risk of loss of acetone. The Ramsay–Young method, though better in some cases than the static methods, is not very good for such solutions because it depends on the rapid evaporation of the substance to cool the thermometer to the b. p. If the solution is not sufficiently rich in volatile constituents, or if their latent heats are not high enough, the thermometer will read high.

EXPERIMENTAL.

The solutions were made up from acetone of "AnalaR" quality (British Drug Houses Ltd.). Before use the alcohols (redistilled if necessary) were tested at the chosen temperature (30°) and shown to have negligible vapour pressure.

The diminution of the partial vapour pressure of acetone with time was observed chiefly in presence of hydrogen chloride (1 ml. of concentrated acid to 35 ml. of the alcohol and 5 ml. of acetone). Since under anhydrous conditions hydrogen chloride catalyses the condensation of acetone to mesityl oxide and phorone, it was important to establish that the concentrated aqueous acid did not of itself slowly lower the partial vapour pressure of acetone in an organic solvent. Experiments were therefore performed with toluene as a solvent, since the deviations from Raoult's law with toluene appear to. be of the same order of magnitude as those with heptyl alcohol as a solvent. Instead of a decrease, however, an increase was noted; this is not yet explained, but is probably connected with the fact that in the toluene–acetone mixtures aqueous hydrochloric acid formed a separate layer whereas in heptyl alcohol–acetone mixtures it did not; the two-phase system would have a higher vapour pressure so long as two phases collaborated in producing it, and this would happen when the transpired air passed through both liquids and stirred them, but not otherwise. The vapour pressure was unchanged for 20 hours at least. The presence of water with the hydrogen chloride, as might be expected on other grounds, serves to prevent loss of acetone by self-condensation.

In the absence of catalysts, the change in vapour pressure with time is within the experimental error of the method. This does not prove that no reaction takes place but may merely indicate that any such reaction is too rapid to be studied by the dynamic method, in which measurements cannot be made less than ½ hr. after mixing. In static measurements by the Bremer–Frowein tensimeter or by the isoteniscope, vapour-pressure readings always increase with time at first and the correct vapour pressure may not be recorded until after 1 or 2 hours. For instance, in a benzyl alcohol–acetone–hydrochloric acid mixture (35, 5, and 1 ml., respectively), in which a decrease in vapour pressure with time would be expected, the tensimeter pressure readings at room temperature (17°) in a large thermostat were 23·3 mm. after 1 hour and 27·9 mm. after 2 hours, and a solution of acetone in water (0·1 mol.-fraction) also at room temperature (17·5°) in a large thermostat gave readings of 31·5, 35·5, 37·5, and 41·0 mm. with the isoteniscope respectively immediately after evacuation, and after 20, 30, and 120 mins.

Menzies (*J. Amer. Chem. Soc.*, 1920, **42**, 978, 1951) pointed out that the sluggishness of the establishment of the vapour pressure in tensimetric measurements had led to error in the system of the tri- and penta-hydrates of copper sulphate. This effect precludes the use of the static method for measurement of vapour-pressure changes during the first 1—2 hours after mixing.

Effect of Time on the Vapour Pressures of Alcohol–Acetone Mixtures containing Concentrated Hydrochloric Acid at 30·8°.—The mixtures contained 35 ml. of alcohol, 5 ml. of acetone, and 1 ml. of acid, the amounts being usually checked by weighing. Measurements were by the dynamic method, except those marked by an asterisk, which were by tensimeter. The results of

Alcohol.	Mol.-fraction of acetone.	Time from mixing.	V. p., mm.	Mol.-fraction of acetone.	Time from mixing.	V. p., mm.
Heptyl	0·183	½ hr.	91·7	0·183	26 hrs.	81·2
	,,	½ hr.	91·2	,,	100 hrs.	79·1
	,,	26 hrs.	82·2			
Benzyl	0·150	1 hr.	40·9	0·150	8 months	33·9
	,,	32 hrs.	39·6	,,	,,	33·9
m-Nitrobenzyl	0·134	1 hr.	27·6 *	0·134	96 hrs.	23·8 *
	,,	1½ hrs.	27·3	,,	7 weeks	23·8 *
	,,	24 hrs.	24·4 *			

experiments at 30·8° are set out in the above table. Every precaution was taken to avoid loss of acetone by evaporation, the reactants being kept either in sealed glass vessels (for the longer experiments) or in stoppered flasks until required for measurement, and in the latter case they were weighed before use to ascertain that no loss had occurred. The acetone content was frequently checked by the author's method of analysis (*loc. cit.*) after the conclusion of the dynamic experiments.

Effect of Catalysts for Fischer's Acetal Synthesis on the Partial Vapour Pressure of Acetone in Benzyl-alcoholic Solution.—To facilitate comparison of the results, they have been calculated from the observed values to 0·1 mol.-fraction of acetone and 30°, on the assumptions that for small ranges of concentration Raoult's law may be applied and that the temperature coefficient of the vapour pressure of acetone is 5% per degree (Rhodes, *loc. cit.*). The mixtures consisted of 35 ml. of benzyl alcohol, 5 ml. of acetone, and the amount of the substance specified in the following table of results. Except where otherwise stated each figure represents a number of concordant results obtained by the dynamic method.

Substance added.	Time after mixing.	V. p., mm.	Substance added.	Time after mixing.	V. p., mm.
None	1 hr.	23·4 *	12·5 G. of $AlCl_3$	2 days	18·65
,,	1½ hrs.	25·2	,, ,,	16 days	19·3 †
,,	22 hrs.	26·25	10 G. of $CaCl_2$	8 days	22·9
1 Ml. of conc. HCl	1 hr.	27·1	Ideal value according to Raoult's law	—	29 2
,, ,,	6 months	21·6			

* Tensimetric measurement after only 1 hr.; therefore low.
† Tensimetric, mean of a large number of results.

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