5. *The Mechanism of the Reaction of Aryl* iso*Cyanates with Alcohols and Amines. Part IV. The Evidence of Infra-red Absorption Spectra regarding Alcohol–Amine Association in the Base-catalysed Reaction of Phenyl* iso*Cyanate with Alcohols.*

By John W. Baker, Mansel M. Davies, and J. Gaunt.

The effect of the addition of various concentrations of triethylamine on the infra-red absorption spectra, in the 3μ region, of methyl and ethyl alcohols in di-*n*-butyl ether and in benzene solutions has been studied by using a Beckman I.R.2 automatic-recording instrument. In the ether solvent the complete absence of the absorption band at 2·74 μ shows that no unassociated OH groups are present, but that the alcohol exists as ether-solvated and self-associated molecules. Addition of triethylamine gives rise to a new absorption in the region of 3·1 μ, which is ascribed to the formation of an amine–alcohol complex of the type postulated on the basis of kinetic studies of the phenyl *iso*cyanate–alcohol reaction in the same medium (Part II, this vol., p. 9).

In benzene solution a strong monomeric OH absorption peak occurs at 2·75 μ and amine addition greatly decreases this absorption with the concomitant incidence of marked absorption in the 3·1 μ region, clearly indicating the formation of an amine–alcohol complex.

The bearing of these results on the kinetic data is briefly discussed.

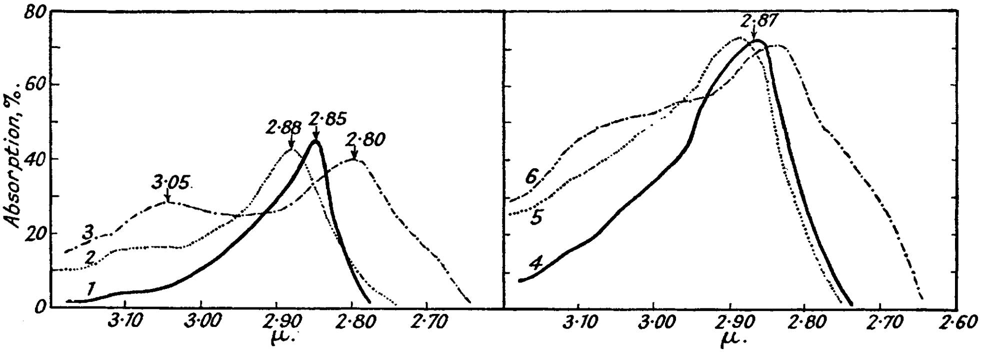
In Part II (this vol., p. 9) it was suggested that the kinetic data obtained in a study of the base-catalysed reaction between phenyl *iso*cyanate and various alcohols could only be satisfactorily interpreted if it were assumed that the tertiary amine catalyst and the reactant, alcohol, form a complex of the hydrogen-bonded type $R_3N \ldots . H \ldots . OR$. Data in the literature regarding infra-red absorption spectra of various amine–alcohol systems provide considerable evidence for such association. For instance, Freymann (*Compt. rend.*, 1937, **204**, 261; cf. *J. Chem. Physics*, 1938, **6**, 497, for summary and bibliography) found that, in solutions of alcohols such as trimethylcarbinol and butyl alcohol in carbon tetrachloride, the overtone band due to unassociated OH disappears on addition of amines such as anilines, pyridine, dibutylamine, etc. It seemed probable, therefore, that examination of the effect of addition of triethylamine on the infra-red absorption spectra of solutions of various alcohols in di-*n*-butyl ether solution, *i.e.*, with the reactants and solvent actually used in the kinetic study, would provide valuable information regarding the molecular condition of the alcohol during the *iso*cyanate–alcohol reaction and test the validity of the mechanism suggested. A preliminary examination has been made of the infra-red absorption spectra of methyl and ethyl alcohols, with and without the addition of triethylamine, in both di-*n*-butyl ether and benzene, in the 3 μ region of the spectrum. Owing to the removal of one of us (M. M. D.) from Leeds, facilities to extend the investigation are no longer available, but the results so far obtained seemed to be of sufficient interest to be placed on record.

Solutions of the single amine and alcohol components as well as amine–alcohol mixtures have been examined. The principal absorptions arise for the hydroxyl group of the alcohol and, in studying these in mixed solutions, corrections have been applied for any slight absorptions due to solvent and amine in the same region.

*Solutions in Di-*n*-butyl Ether.*—The absorption curves for methyl alcohol and methyl alcohol–triethylamine mixtures are given in Fig. 1. Methyl alcohol alone at a concentration of 0·4M (curve 1) shows a single, well-defined absorption centred at 2·85 μ. The centre of this absorption moves to slightly longer wave-lengths, and the breadth of the band increases considerably in that direction, when the concentration is increased to 1·0M (curve 4). Dilute solutions of the alcohol in "inert" solvents (*e.g.*, carbon tetrachloride, chloroform, or carbon disulphide) show a strong absorption near 2·73 μ due to unassociated hydroxyl groups, and, at higher concentrations, a further broad band, due to associated hydroxyl, appears at 2·95 μ. The absence of any absorption in the 2·73 μ region in the di-*n*-butyl ether solution clearly shows the absence of unassociated alcohol molecules in this solvent. The position and form of the absorption at 2·85 μ indicate a distinct interaction between the alcohol and the solvent ether, such solvation giving rise to a frequency change of only about half that which occurs on self-association of the alcohol. Correlating the extent of the frequency shift with the energy of solvation, it may safely be concluded that the energy of solvation of the alcohol by the ether is less than that of the self-association process, which is 4·7 kcals. per g.-mol. (Mecke and Nückel, *Naturwiss.*, 1943, **31**, 248).

FIG. 1.

Infra-red absorption of MeOH–NEt_3 *in di-*n*-butyl ether solutions.*



1. 0·4M-MeOH.
2. 0·4M-MeOH + 0·4M-NEt_3.
3. 0·4M-MeOH + 1·0M-NEt_3.

Cell width = 0·10 *mm.*

4. 1·0M-MeOH.
5. 1·0M-MeOH + 0·4M-NEt_3.
6. 1·0M-MeOH + 1·0M-NEt_3.

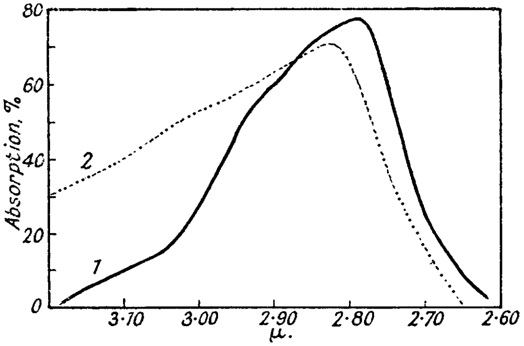
Cell width = 0·10 *mm.*

Addition of 0·4M-triethylamine to the methyl alcohol solutions at either 0·4 (curve 2) or 1·0M (curve 5) concentration causes no *pronounced* change. There is a slight shift (~0·025 μ) of the whole absorption band in the direction of longer wave-lengths when the amine is present, accompanied by a slight increase in absorption intensity in the 3·05—3·1 μ region. It is doubtful whether the former effect can be ascribed to anything more specific than the change in the medium brought about by the presence of the amine, but it is possible that the increase in absorption near 3·1 μ is due to the formation of some amine–alcohol complex. This possibility is strengthened by the form of the absorption curve for the same alcohol concentrations in the presence of 1·0M-concentration of triethylamine (curves 3 and 6). With equimolecular (1·0M) concentrations of alcohol and amine a distinct shoulder is detectable in the 3·1 μ region (curve 6), which becomes a small, but definite peak at ~3·05 μ when the amine is present in excess (curve 3).

Even in this case, however, the absorption is still weaker than is that of the ether–alcohol association, suggesting that the latter probably remains the predominating form of the alcohol component. On the basis of the identification of the 3·1 μ absorption with an alcohol–amine complex, its position suggests that the energy of the amine interaction with the hydroxyl group is of the same order or possibly slightly greater than is that of the self-association of the alcohol, the band corresponding to which is at 2·95 μ.

FIG. 2.

Infra-red absorption of EtOH–NEt$_3$ *in di-*n*-butyl ether solutions.*

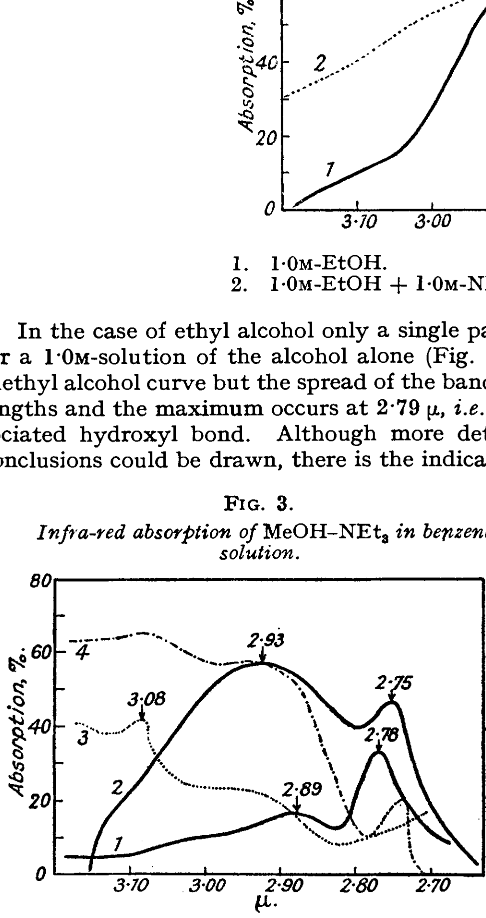


1. 1·0M-EtOH.
2. 1·0M-EtOH + 1·0M-NEt$_3$. *Cell width* = 0·10 *mm.*

In the case of ethyl alcohol only a single pair of absorption curves has been studied. That for a 1·0M-solution of the alcohol alone (Fig. 2, curve 1) shows the same general form as the methyl alcohol curve but the spread of the band is rather greater in the direction of longer wavelengths and the maximum occurs at 2·79 μ, *i.e.*, considerably nearer to the position of the unassociated hydroxyl bond. Although more detailed examination is necessary before positive conclusions could be drawn, there is the indication that the solvent–alcohol association may be rather less in the case of ethyl alcohol than it is with methyl alcohol, and some unassociated alcohol may be present. Addition of 1·0M-triethylamine (Fig. 2, curve 2) again causes a slight displacement of this maximum to 2·83 μ and a significant increase in absorption in the 3·1 μ region, which is probably associated with amine–alcohol complex formation.

FIG. 3.

Infra-red absorption of MeOH–NEt$_3$ *in benzene solution.*

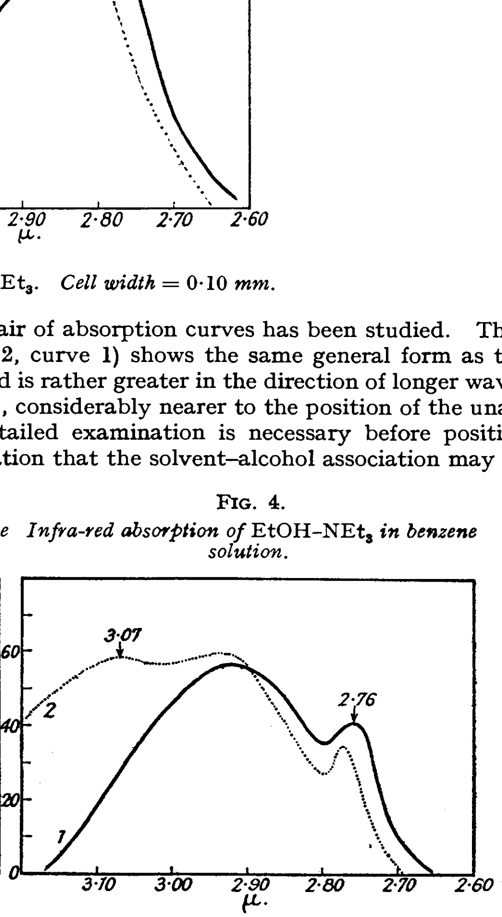


1. 0·4M-MeOH.
2. 1·0M-MeOH.
3. 0·4M-MeOH + 1·0M-NEt$_3$.
4. 1·0M-MeOH + 1·0M-NEt$_3$.

Cell width = 0·10 *mm.*

FIG. 4.

Infra-red absorption of EtOH–NEt$_3$ *in benzene solution.*



1. 1·0M-EtOH.
2. 1·0M-EtOH + 1·0M-NEt$_3$.

Cell width = 0·10 *mm.*

These preliminary investigations do show that, in di-*n*-butyl ether, *i.e.*, under the reaction conditions used in the kinetic study, there is considerable association of the alcohol with the solvent and possibly with itself, and that amine–alcohol complex formation does occur. Both are probably more pronounced with methyl than with ethyl alcohol.

Solutions in Benzene.—Striking differences are observed when the same alcohol–amine systems are examined in solution in dry benzene. The infra-red absorption curves for methyl alcohol are shown in Fig. 3. At both 0·4 and 1·0M-concentrations (Fig. 3, curves 1 and 2) the alcohol clearly shows the two characteristic absorptions due to unassociated (~2·75 μ) and associated (2·90 μ) molecules. Addition of triethylamine causes a marked decrease in the intensity of the monomeric absorption (Fig. 3, curves 3 and 4) and, in the presence of an excess of the amine, it is almost completely obliterated. The alcohol " association band " is not greatly influenced at the amine concentrations studied, but a distinct absorption is now clearly observed in the 3·1 μ region. The exact centre and intensity of this absorption were not accurately determined, since the solvent itself shows increasing absorption just beyond this wavelength, but it is established that an alcohol–amine interaction occurs in benzene solution with even more marked spectroscopic effects than in di-*n*-butyl ether, and it is regarded as extremely probable that it is this interaction product which is responsible for the 3·1 μ absorption.

Corresponding infra-red absorption curves for ethyl alcohol are given in Fig. 4. The same general features are apparent except that the amine–alcohol absorption (at 3·07 μ) is rather less pronounced. This observation is in harmony with the known weaker acidity of ethyl compared with methyl alcohol, a factor which would be unfavourable to amine–alcohol complex formation of the hydrogen-bonded type.

Thus these preliminary spectroscopic results do lend support to the hypothesis which was developed in Part II (*loc. cit.*) on the basis of the kinetic data, and their implications on the effect of a change of solvent on the *iso*cyanate–alcohol reaction are immediately apparent. Data relating to such a kinetic study in benzene solution are discussed in Part V (following paper).

EXPERIMENTAL.

Preparation of Materials.—The specimens of methyl and ethyl alcohol, triethylamine, and the solvent di-*n*-butyl ether were the carefully purified and dried samples previously used in the kinetic studies (Part II, *loc. cit.*). Each sample was freshly redistilled just before the solutions were made up for examination.

"AnalaR" Benzene was refluxed for 6 hours over phosphoric oxide and then fractionated through a Widmer column with exclusion of atmospheric moisture. The fraction of constant b. p. was refluxed over sodium until no further action occurred, again fractionated, and the sample, b. p. 79·8°, was stored over fresh sodium wire in a glass-stoppered flask. Small quantities of this sample were freshly distilled immediately before use.

The solutions used for the study of the infra-red absorption were made up by direct weighing from a weight pipette, using calibrated graduated flasks, immediately before use.

Infra-red Absorption Curves.—The spectrometer used was a Beckman I.R.2 instrument incorporating a 60-mm. base rock-salt prism, which records directly, on an 11-inch chart, the energy transmitted as the spectrum is traversed. The effective slit widths were at the most 0·020 μ, and a 0·10-mm. thick rock-salt cell was used throughout. The cell compartment was at 28° ± 2°. Percentage absorption was determined by the convenient method of Willis and Philpotts (*Trans. Faraday Soc.*, 1945, **41**, 187) and, in every case, the curves have been corrected for the small absorption of the solvent and the amine in the region studied.

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